PB-238 921

DEVELOPMENT OF SAMPLING DEVICES FOR GASEOUS ATMOSPHERIC TRACERS

C. L. Deuel, et al

Analytical Research Laboratory, Incorporated

Prepared for:

National Environmental Research Center

July 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-650/4-74-050	2.
3. PB 238 921	
4. TITLE AND SUBTITLE: Development of Sampling Devices for Gaseous Atmospheric Tracers	5. REPORT DATE: July 1974
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): C. L. Deuel and R. M. Roberts	8. PERFORMING ORGANIZATION REPORT NO.: 2601-F
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Analytical Research Laboratories, Inc. 160 Taylor St. Monrovia, Ca. 91016	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.: 68-02-1235
12. SPONSORING AGENCY NAME AND ADDRESS: EPA, National Environmental Research Center Research Triangle Park, N. Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED: Final Report 6/1/73-6/1/74
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report discusses the development and testing of an air sampler to be used to collect over protracted periods and to facilitate the measurement of atmospheric tracer compounds released in meteorological diffusion studies. Tests were conducted to determine the adsorptive capacity of various sorbents potentially suitable for collecting such electronegative tracer compounds as SF_6 and CF_3SF_5. A field-practical sampler, incorporating the best sorbent found, a high surface-area coconut charcoal, was then designed and subjected to laboratory tests. The effects on sampler performance of various atmospheric influences, such as composition, pollutants, temperature, and tracer loading and level were determined. Desorption techniques allowing quantitation of the tracer were developed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air pollution, tracer, sorption, measuring instruments, gas sampling, gas detectors, trace elements, electronegativity.	Atmospheric tracers, electrophilic materials	7/D, 13/B, 14/B

Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE US Department of Commerce Springfield, VA. 22151

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT: Unrestricted	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 64
	20. SECURITY CLASS (This page): Unclassified	22. PRICE: 4.25 - 7.25

EPA Form 2220-1 (9-73)

EPA-650/4-74-050

DEVELOPMENT OF SAMPLING DEVICES FOR GASEOUS ATMOSPHERIC TRACERS

by

C. L. Deuel and R. M. Roberts

Analytical Research Laboratories, Inc.
Monrovia, California 91016

Contract No. 68-02-1235
ROAP No. 26AAI
Program Element No. 1AA003

EPA Project Officer: Francis Pooler, Jr.

Meteorology Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

July 1974

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

This report discusses the development and testing of an air sampler to be used to collect over protracted periods and to facilitate the measurement of atmospheric tracer compounds released in meteorological diffusion studies. Tests were conducted to determine the adsorptive capacity of various sorbents potentially suitable for collecting such electronegative tracer compounds as SF_6 and CF_3SF_5. A field-practical sampler, incorporating the best sorbent found, a high surface-area coconut charcoal, was then designed and subjected to laboratory tests. The effects on sampler performance of various atmospheric influences, such as composition, pollutants, temperature, and tracer loading and level were determined. Desorption techniques allowing quantitation of the tracer were developed.

This report was submitted in fulfillment of contract number 68-02-1235 by Analytical Research Laboratories, Inc., under the sponsorship of the Environmental Protection Agency. Work was completed as of June, 1974.

CONTENTS

		Page
Abstract		iii
List of Figures		iv
List of Tables		v
Sections		
I.	Conclusions	1
II.	Recommendations	3
III.	Introduction	4
IV.	Test Program	7
	Laboratory Test System	7
	Adsorbent Screening Approach	11
	Adsorbent Screening Results	14
	Site Competition Studies	17
	Influence of Temperature on Adsorber Capacity	20
	Other Atmospheric Tracers Tested	22
	Atmospheric Tracers Response and Calibration	24
	Atmospheric Tests	24
	Effect of Concentration on SF_6 Adsorption	30
	Analytical System	31
	Stripping Tracer from Sampler	32
	Samplers	39
	Field Operation Requirements	54
V.	References	56

FIGURES

No.		Page
1	Laboratory Test System - Flow Diagram	8
2	Laboratory Test System - Front View	9
3	Laboratory Test System - Back View	10
4	Retention Volume of SF_6 on Type AC Charcoal	21
5	Retention Volume of Freon 11 on Type AC Charcoal	23
6	Retention Volume of CF_3SF_5 on Type AC Charcoal	26
7	Linear Portion of Calibration Curve for SF_6	27
8	Calibration Curve for CF_3SF_5	28
9	ECD Response of 3×10^{-10} g Standard SF_6 Sample	33
10	ECD Response of Duplicate 3×10^{-10} g SF_6 Samples Following Charcoal Adsorption-Desorption	34
11	Sampler Desorption Unit	35
12	Field-Type Tracer Sampler	41
13	Field-Type Tracer Sampler with Adsorption Tubes in Place	42
14	Disassembled Field-Type Tracer Sampler with Adsorption Tubes Removed	43
15	Field-Type Tracer Sampler with Desorption Unit	44
16	Atmospheric Tracer Sampler Sketch	46
17	Sampler Body - Side View	47
18	Sampler Body - End Views	48
19	Atmospheric Tracer Sampler - Side-View Photograph	50
20	Atmospheric Tracer Sampler - End-View Photograph	51
21	Atmospheric Tracer Sampler, Assembled for Field Testing	52

TABLES

No.		Page
1	SF_6 Capacity of Various Adsorbents, µg/g	15
2	Effect of Hydrocarbon Mixture on V_R of SF_6 on Type AC Charcoal at 24°C	19
3	Comparison of the Retention Volume (V_R) of SF_6 on One Lot of Type AC Charcoal at Various Temperatures	25
4	Sulfur Hexafluoride Desorption Recovery Data	38
5	Desorption Recovery Data for CF_3SF_5	40
6	Atmospheric Tracer Sampler - Parts List	49

SECTION I

CONCLUSIONS

Sulfur hexafluoride, the lowest boiling of the atmospheric-tracers, is not retained well by any adsorption media. Of the materials tested, only charcoal was found to retain this compound sufficiently well to permit sampling at expectable tracer levels for the sought-for period of 4 hours.

There is considerable difference in the isothermal capacity of various charcoals and even the same charcoal, when in different conditions, to adsorb SF_6 and other tracers. Activation prior to use is mandatory if maximum sorptive capacity is to be realized.

Charcoal was found not to be irreversibly affected by large doses of acid vapors, atmospheric pollutants, water, and other atmospheric components.

Input of large quantities of water and hydrocarbons into the sampler will affect its capacity for SF_6 and other tracers. If sufficient charcoal is incorporated in the sampler, worse-case situations can be compensated for. Removal of particulates, water, and most hydrocarbons from the atmospheric sample stream are, however, successfully accomplished by the precolumn trap incorporated within the sampler itself.

Quantitative collection of SF_6 and other tracers over a 4 hour sampling period with a time-averaged tracer level as unrealistically high as 0.1 ppm can be accomplished at air temperatures as high as $40^{\circ}C$ ($104^{\circ}F$).

Vacuum/thermal stripping is necessary for quantitatively removing SF_6 from the charcoal sampler. Analytical error considered, 100% recoveries by this approach are readily achievable.

The use of a charcoal column in the chromatograph used for quantitating the desorbed sampler contents separates the SF_6 and other

tracers from any hydrocarbons desorbed from the sampler. This column can readily be backflushed to avoid contamination of the detector.

The sampler, when used as recommended, will perform for up to 100 sampling operations, involving different urban environmental conditions, without evidence of performance decay.

The short linear dynamic range of the conventional electron capture detector (ECD) makes tracer quantitation unnecessarily involved. The broader-range (constant current) Maggs ECD system now commercially available would greatly facilitate such measurements.

SECTION II

RECOMMENDATIONS

This program was limited to laboratory study and development. Although polluted urban air was routinely employed, it was not within the scope of the contract to conduct widespread field tests to verify the laboratory results. It is therefore recommended that field tests be performed using suitable verification systems. The sampler developed on the program, which is not a deliverable item, would be donated for this purpose.

The development of the extended-range Maggs ECD will greatly enhance the measurement of tracers in time-integrated samples. The great sensitivity of the conventional ECD is normally of no value with such samples and, in fact, large dilutions must be practiced to bring the desorbed tracer within linear ECD range. The Maggs ECD would largely obviate such manipulations and should be evaluated in any further test work performed with the ARLI sampler design.

SECTION III

INTRODUCTION

OBJECTIVES

With the growth of urbanization and its associated industrialization, it has become increasingly imperative for man to control his environmental pollution. To develop the principles and mechanisms necessary to achieve effective air pollution control, the diffusion of pollutants must be determined. The number and complexity of the variables affecting the movement of air pollutants, including the chemical and physical nature of the pollutants, the structure of the air pathways, local topography, and prevailing meteorology, are such that mathematical modeling and computer calculations are necessary for the prediction of pollution patterns.

Monitoring of specific pollutants provides valuable information concerning the overall distribution of a specific pollutant, but, since the monitored chemical will have originated from many sources, is of limited value in pinpointing emittors. In order to associate pollutants with their sources, unique inert chemical tracers that can be detected at very low concentrations are frequently released to the atmosphere at points of interest. Compounds generally employed are those of the generic groups of electronegative compounds incorporating S-F or C-F structures. These compounds tend to be low boiling, non-toxic, odorless, colorless, chemically stable, are easily dispersed into the atmosphere, are not likely to be present in normal atmospheres, and can be readily measured with the ECD in the parts per billion range.

The very characteristics that make such compounds invaluable as atmospheric tracers for instantaneous detection prevents their effective field use when time-integrated concentrations need to be known. To date, large evacuated containers fitted with calibrated slow leaks have been the only functional means of collecting time-averaged gaseous tracer samples. A more ideal system that fulfills the criteria for

extended-time sampling periods would be based upon adsorption methods. In this type of system, the tracer-containing air stream would be passed through a column containing the adsorption medium. The tracer would be retained on the adsorbent over the sampling interval, after which the column would then be sealed and preserved for conventional analysis at a later time in the laboratory.

The purpose of this program then was to develop and test a small, light weight sampler compatible for operation with conventional field gear, such as gas pumps etc. This device would be capable of collecting atmospheric tracers, such as sulfur hexafluoride (SF_6) and trifluoromethylsulfur pentafluoride (CF_3SF_5), at levels ranging from the limit of ECD detectability to four magnitudes of higher concentration. The sampler would be capable of operating for sampling intervals ranging from a few minutes to several hours. The device would be capable of sampling under adverse atmospheric conditions, including those of temperature, humidity, and pollutant (including particulate) levels. The sampler would be of a reusable configuration and be capable of extended cycle usage without decay of performance.

SUMMARY OF RESULTS

Initial experimentation involved the screening of twenty possible adsorbents to determine their retention capacity for tracers. Sulfur hexafluoride was used exclusively in this process since not only is it the most universally used, it is the most difficult to retain. The materials investigated included porous polymer beads (both coated and uncoated), various combinations of fluoroethylene polymers and fluorinated coatings, desiccant materials, catalytic substances, and various activated charcoals. Of these, only activated charcoal was found to retain SF_6 in quantities sufficient to satisfy program requirements. The sorptive capacity of the charcoal selected for the sampler was measured as >1 mg SF_6 per gram charcoal. Based on maximum atmospheric tracer levels expected and sampling period (4 hrs) at design flow rate (25 cc/min), a capacity for 10^{-8} g SF_6 was the projected requirement.

After a suitable adsorbent was found, the effects of atmospheric pollutants were examined at various concentrations and temperatures. These included such constituents as hydrocarbons, carbon monoxide, oxides of nitrogen, oxides of sulfur, and water. Urban air was also used as the tracer diluent in a series of verification sampling tests.

In addition to SF_6, other tracers including various Freons and a new EPA developed compound, CF_3SF_5, were studied for retention volume and recovery.

After determining that Barnebey-Cheney Type AC activated charcoal would retain sufficient quantities of SF_6 for time-integrated sampling, methods for recovery and quantitation of the tracers were developed. By use of vacuum thermal stripping in combination with cryogenic trapping, essentially 100% recoveries were regularly achieved. The recovered quantities generally were sufficiently large to exceed the range of linear response of the ECD's used. Dilution of these concentrated samples was necessary to achieve quantitation of the recovered tracers.

The final sampler design recommended consists of a train commencing with a Millipore filter (for the removal of particulates), followed by a reservoir of mixed adsorbent/desiccant to remove water and many hydrocarbons, then a U-tube filled with ground, screened, activated charcoal.

SECTION IV

TEST PROGRAM

LABORATORY TEST SYSTEM

A gas train system, Figures 1 to 3, was constructed for evaluation of the candidate adsorbents. The hardware consisted of stainless steel Hoke toggle valves with Kel-F seats, Brooks flow controllers, and stainless steel lines, all mounted on a 25 x 750 cm panel. Separate input lines were provided for the premixed tracer, diluent gas, hydrocarbon, NO_x, and SO_x gas mixtures. Flow rates were individually set through the flow controllers and/or needle valves and were measured by a bubble flow meter.

At the beginning of the train, a standard fritted-glass gas scrubber was installed to furnish gas humidification. Because the system was operated above atmospheric pressure, humidification to 100% saturation was not possible, but this limitation was not considered to be significant. Moisture was introduced at the head of the train because: (1) if the air contaminants to be added in controlled amounts to the stream were to react with each other or with water, no products would be formed that would not be formed in water saturated air; and (2) the use of a bubbler after the addition of the other ingredients would result in loss of some of the gases, especially NO_x and SO_x.

The accumulator consisted of a short column of the adsorbent of interest. This unit was either placed in a Transite container with nichrome wire heaters and a thermocouple temperature readout for high temperature operation, or immersed in a dewar with a suitable coolant for low temperature studies.

The cryotrap system consisted of multiple loops of 3.2 mm SS tubing having an internal volume of ~7 cc. These loops allowed the gas flow to pass into and out of the cryogenic fluid several times to break up aerosols and furnish essentially 100% trapping efficiency.

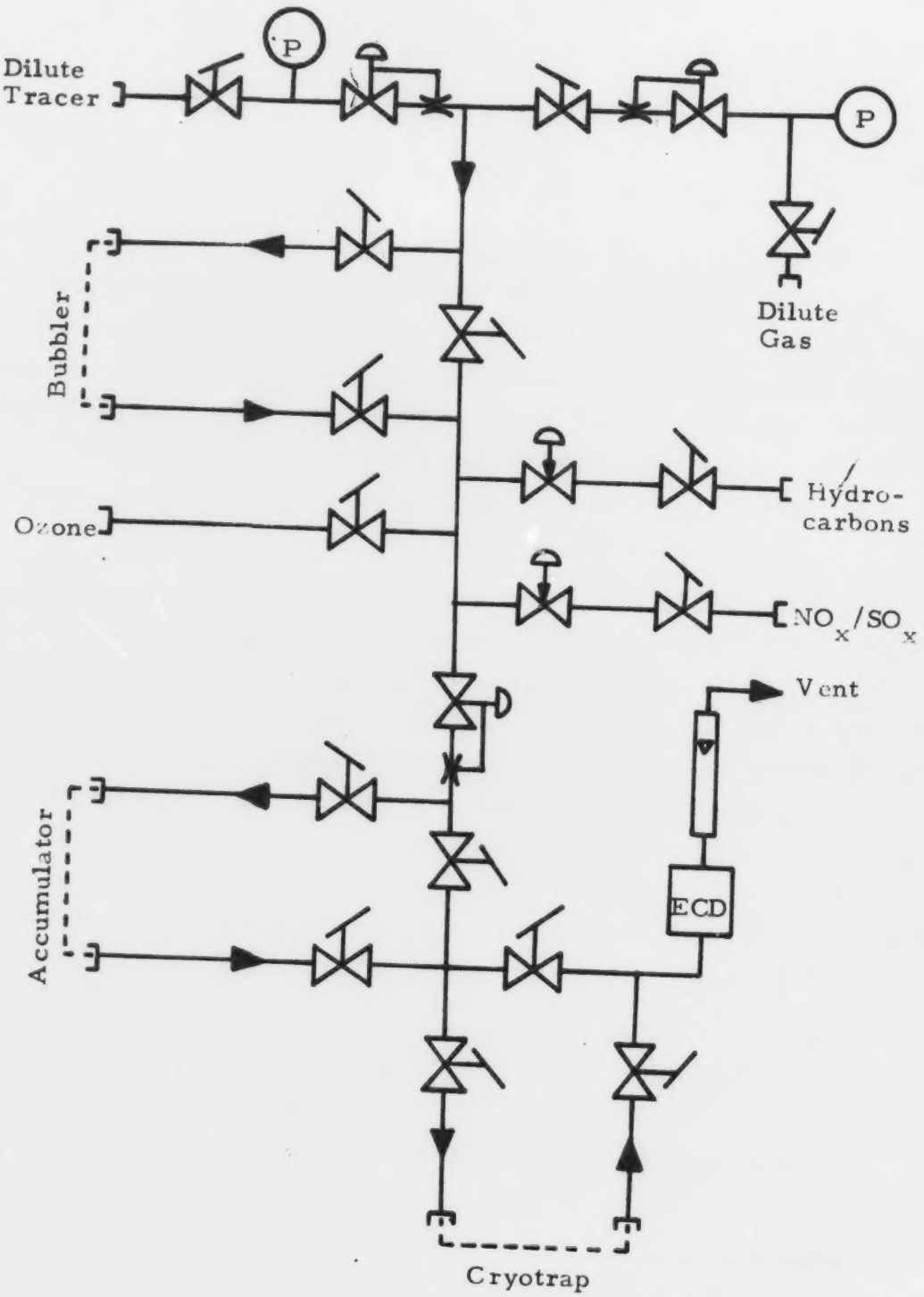


Figure 1. Laboratory test system - flow diagram

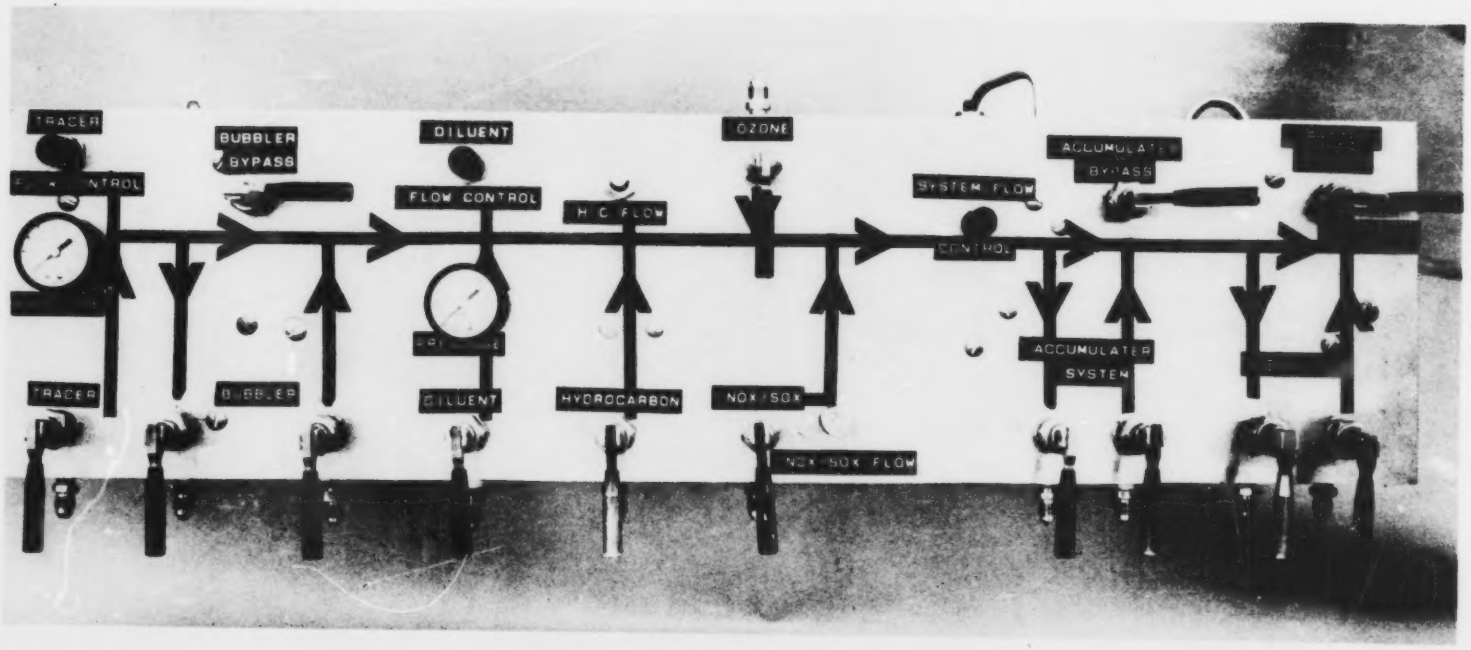


Figure 2. Laboratory test system - front view

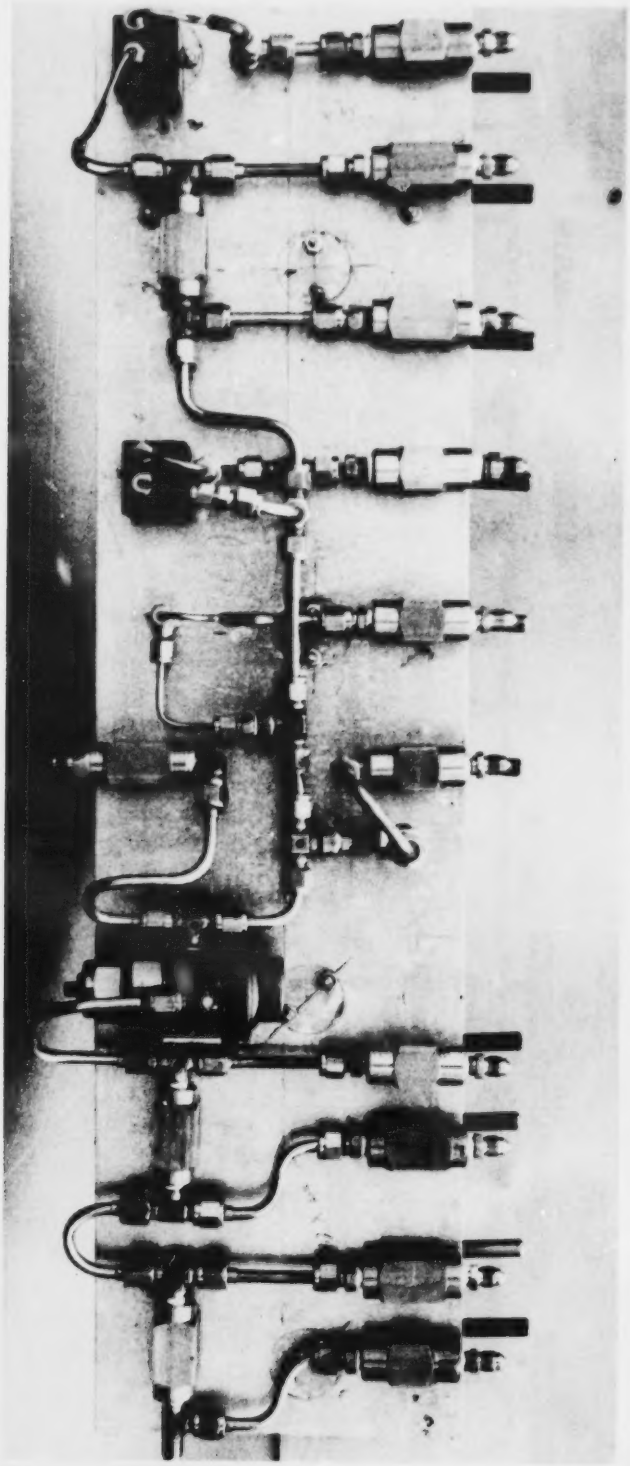
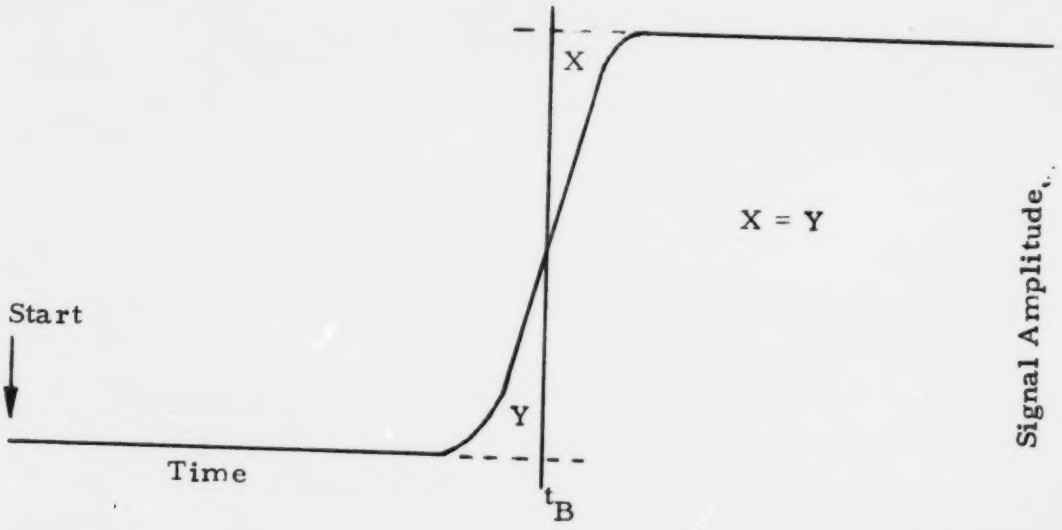


Figure 3. Laboratory test system - back view

The detector used for the adsorbent screening studies was a tritium foil ECD originally designed for use with a P&E Model 880 gas chromatograph. Since this detector was designed as a hang-on unit, it was well suited for incorporation into the gas train.

ADSORBENT SCREENING APPROACH

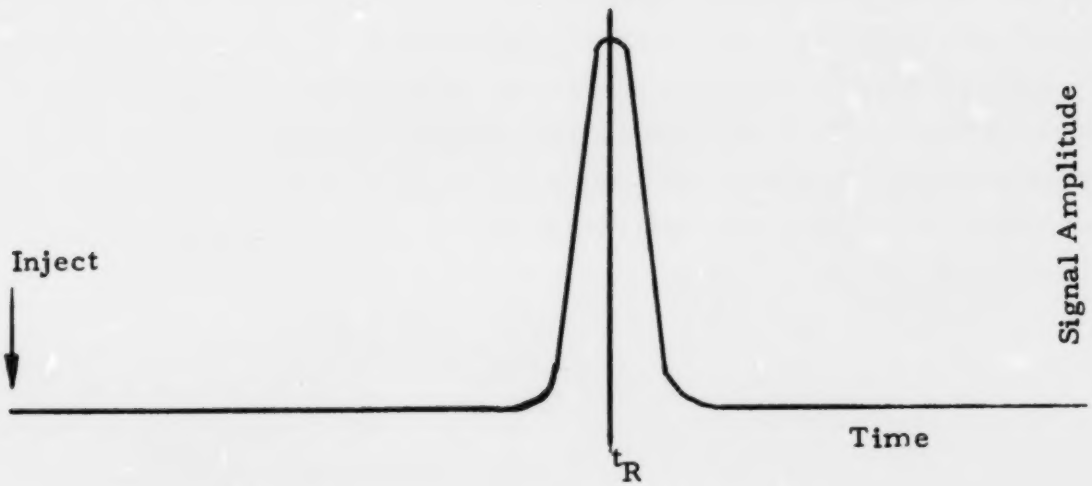
An obvious approach to conducting evaluation tests of candidate adsorbents would be to pass tracer-containing gas through them until breakthrough occurs. This is essentially a simple form of frontal analysis. If the tests are conducted within the linear portion of the adsorption isotherm and since irreversible adsorbents would be excluded, the tracer concentration would not be important. Thus the capacity of each candidate could be related to the breakthrough volume, V_B, or the air flow-rate times the time to breakthrough, t_B. The latter is usually graphically defined as the vertical intercept of the breakthrough signal front that furnishes equal area segments formed by the intercept, the signal, and tangents to the baseline and plateau of the signal, viz:



FRONTAL ANALYSIS BREAKTHROUGH POINT

If, at breakthrough, the tracer were eliminated from the input gas, it would take in excess of an additional t_B for all of the tracer remaining on the adsorbent to come off. Although the stripping process can of course be expedited, frontal analysis is not a convenient approach.

For screening purposes, one need only inject a small volume of the tracer-containing gas that would have been used for frontal analysis. If the carrier flow rate is the same, the signal for the discretely injected sample will, under ideal conditions, occur at the same time (retention time or t_R) as t_B, viz:



GAS CHROMATOGRAPHIC ANALYSIS SIGNAL TRACE

This is to say that retention volume, V_R, which is flow rate times t_R, is equal to V_B. This equivalence, which is well known to gas chromatographers and has been mathematically derived from basic principles, is conditional. The factors that can introduce offsets are not important in the present context, however, and can be ignored for purposes of preliminary screening work. In the text that follows

the terms breakthrough and retention volume or V_B and V_R are thus interchangeably used.

Because V_B and V_R are determined by the dead volume within the adsorber device tested, the quantity of active material packed therein, and other factors, use of a capacity term would be more definitive. This would permit the comparison of the adsorbents screened on the basis of weight of tracer retained per unit weight of adsorbent. Determination of ultimate capacity, however, would have no significance for the present work since the tracer concentrations required would far exceed the micrometeorological test situation. For the adsorbent screening evaluations described here, therefore, the capacity values given are relative to the input concentration employed. That is, capacity equals tracer concentration times V_R divided by the weight of adsorbent used.

A commercially prepared and analyzed mixture of 0.9 ppm SF_6 in nitrogen was purchased for this program. For adsorbent screening purposes, however, a 50 ppm mixture of SF_6 in nitrogen was prepared and used. Nitrogen rather than air was selected as the diluent because of the necessity for continuous monitoring for breakthrough with the ECD. The latter produces an appreciable signal for oxygen.

For testing, a series of small adsorption tubes each 500 x 3.2 mm were packed with the sorbent of interest. These tubes each contained about 0.7 g of active packing.

Retention volume studies were made by establishing a steady state base line with nitrogen carrier gas flowing through the adsorber. A "small" sample of SF_6, consisting of 1 or 2 cc of 50 ppm SF_6 in nitrogen, was then introduced into the carrier stream. The retention volume, V_R, was calculated as the product of the elapsed time from the introduction of the sample to the maximum detector response and the flow rate in cc/min. In tests to verify that $V_R = V_B$, the nitrogen carrier stream was stopped and a stream of nitrogen containing

SF_6 substituted. The appearance of a signal at breakthrough required, within experimental error, the same volume of gas.

In addition to simplifying the preliminary screening work, the slug addition of tracer to measure V_R saved time in clearing the adsorbers of tracer and helped maintain a low tracer level in the laboratory air.

ADSORBENT SCREENING RESULTS

Table 1 contains a listing of the observed SF_6 capacities for the various adsorbents tested on this program. The porous polymer Porapak series comprises various crosslinked polymers which have found universal acceptance in gas chromatographic applications. Of these, Porapak P, a styrene-divinylbenzene copolymer is the least polar, while Porapak T has a crosslinkage of ethylene glycol dimethacrylate, making it the most polar of the series. Porapak Q, ethylvinylbenzene-divinylbenzene, is slightly more polar than P, while Porapak N, containing vinyl pyrollidone, is slightly less polar than T. There were no appreciable differences in the SF_6 capacity of any of the polymer beads, and certainly no pattern of capacity that related to polarity. Polypak II was an early contribution of Hewlett-Packard to the porous polymer bead adsorbent field. This material is quite similar to Porapak Q. Since the porous polymers are readily liquid coated, the Polypak II was coated with 10% tetrahydroxyethylethylenediamine (THEED). This coating improved the retention of SF_6, but was still much less than the poorest of the activated charcoals. Tenax, another porous polymer with a 2,6-diphenyl-p-phenylene oxide base, exhibited very low capacity for SF_6. Carbosieve B is a charcoal with controlled pore size that performs much as molecular sieves. Like the latter, it too furnished only minimal retention of SF_6.

Dietz and Cole[1] have reported evidence of SF_6 adsorption on Teflon thread sealant tape and on Teflon valve components. Based upon this report, a series of adsorbers involving a variety of fluorocarbons was prepared. Fluoropak 80 and Teflon VI, both finely divided Teflon powders, showed little affinity for SF_6. A partially fluorinated substance

TABLE 1. SF_6 CAPACITY OF VARIOUS ADSORBENTS
($\mu g/g$)

Adsorbent	SF_6 Capacity
Barnebey-Cheney type AC charcoal, activated	1022
Witco 888 Charcoal, activated	546
Barnebey-Cheney type AC charcoal, as received	404
Barnebey-Cheney type GI charcoal, as received	221
Polypak II with 10% THEED[a]	11.9
Porapak T	10.4
Porapak P	8.9
Porapak Q	8.3
Porapak N	7.5
Fluoropak 80	7.5
Teflon VI	6.0
Carbosieve B	4.4
Kel-F 300 L.D.	3.0
Tenax GC	3.0
Fluoropak 80 with 5% carbowax 4000 and 2% carbowax 600	0.3
Diatomaceous earth with 15% Fluorolube and 5% Kel-F 300 L. D.	0.3
5A Molecular Sieve	8.5
Silica gel	10.7
Hopcalite	< 1
Calcium chloride	< 1
Lithium hydroxide	< 1

[a] tetrahydroxyethylethylenediamine

Kel-F 300 L.D., proved to have even less capacity. To achieve a more intimate contact, an adsorption tube packed with diatomaceous earth coated with partially fluorinated Fluorolube and Kel-F 300 was prepared. This and a similar tube containing Fluoropak 80 coated with carbowax had the least adsorption of SF_6 of all candidates tested.

Of the adsorbents tested, only the activated charcoals retained SF_6 in sufficient capacity to permit long term sampling. These charcoals were ground and screened, with the 40-60 mesh cut being retained for use. Two Barnebey-Cheney coconut shell charcoals, types AC and GI, were tested as received. The type AC indicated nearly twice the capacity of type GI.

A petroleum-based charcoal, Witco 888, was ground, screened, and activated in a vacuum oven at 280°C for 8 hours. The apparent capacity for SF_6 was greater than 0.5 mg/g. A second lot of type AC charcoal was then ground and screened. The 40-60 mesh cut was activated in a vacuum oven at 280° for 8 hours. Activation more than doubled the capacity of type AC over the as-received condition. An SF_6 capacity value of 1.02 mg/g was calculated. Based upon test values obtained by Turk and coworkers[2], one gram of activated, type AC charcoal should retain all of the SF_6 contained in over 15 cubic meters of air when at concentrations of 11 ppb. Obviously, such large volumetric samplings are not required in the present context, but the capacity reported does tend to corroborate its selection, as was done on the present program.

A series of reactive materials were also considered for potential use in the removal of possibly interfering air constituents. These consisted of hopcalite (a group of metal oxides) for CO conversion, calcium chloride and magnesium perchlorate for water abstraction, lithium hydroxide for CO_2 and, possibly, NO_x/SO_x removal, silica gel and 5A molecular sieve for organic s and water removal. All materials were ground and screened so they could be readily packed in a 50x0.32 cm adsorption tube. The hopcalite, lithium hydroxide and calcium chloride tests all indicated retention volumes only

slightly greater than the system dead space. The magnesium perchlorate sample adsorbed sufficient moisture to cake and plug the adsorption column. Silica gel and 5A molecular sieve both retained very little SF_6, with retention volumes comparable to those obtained from porous polymer beads.

SITE COMPETITION STUDIES

Air constituents considered as possibly having deleterious effects upon the adsorption of atmospheric tracers were carbon monoxide, carbon dioxide, water, hydrocarbons, and the oxides of nitrogen and sulfur. A series of mixtures of CO, CO_2, NO_2, SO_2, and CH_4 in nitrogen were prepared, each at ~325 ppm. Introduced into the gas train, a 20cc/min flow from any of the mixed gases, when blended with the 90 cc/min nitrogen carrier flow, resulted in a concentration of ~60 ppm in the system. With the possible exception of CO and CO_2, these levels were considerably greater than would be expected in air. Ozone was omitted because it is instantaneously eliminated by charcoal.

A series of determinations established a 24°C retention volume (V_R) of 2500 cc for the type AC charcoal adsorber used for these tests. To determine the effect of each contaminant, a sample of SF_6 was added to the carrier stream composed of the ~60 ppm dilution of the appropriate chemical as described. Each of the contaminant mixes in turn was blended with the nitrogen carrier. The V_R for SF_6 remained at a constant 2500 cc despite the presence of the other components except methane, which caused the V_R for SF_6 to be reduced to 2450 cc. Combinations of mixes were also introduced into the carrier with no detectable changes in SF_6 adsorption capacity, except again, for a slight decrease when methane was present in the mixture. Finally, to simulate a very dirty air sample, all the pollutants were combined together in the carrier stream. The V_R for SF_6 was reduced to 2460 cc, a reduction of less than 2%. Following these tests, the V_R for SF_6 was checked using uncontaminated carrier. It was found to be normal at 2500 cc. Analyzing these test results, it would seem that of the contaminants chosen methane alone offers adsorption site com-

petition with SF_6. Subsequent tests indicated methane had a retention volume of 100 cc on the adsorption column tested.

Partially because of the low retention volume of methane and to test for the effects of the various classes of hydrocarbons, a mixture of nominally 180 ppm each of representative n-alkanes (propane) branched alkanes (neopentane), alkenes (cis and trans isomers of 2-butene), aromatics (benzene), oxygenated hydrocarbons (methyl alcohol), and chlorinated hydrocarbons (chloroform) was prepared in nitrogen. This mixture was blended with the carrier stream at a 1:9 ratio. After a series of SF_6 retention determinations, it was noted that the retention volume for SF_6 at 25°C had dropped from an initial 2200 cc to 1150 cc.

A fresh mixture of the six hydrocarbons representing the various classes was prepared at 300 ppm in nitrogen. A fresh adsorber column loaded with type AC charcoal that had been activated by thermal-vacuum stripping at 285°C for 8 hours was prepared. This column had a retention volume for SF_6 of 3325 cc at 24°C. A series of tests were performed in which the V_R of SF_6 was first determined using uncontaminated nitrogen carrier. Following this, a determination of the V_R of SF_6 was made with the hydrocarbon mix blended into the carrier stream at a 1:6 ratio to produce a 50 ppm level of each contaminant. These tests were followed by a series of 8 additional V_R determinations, in which pure nitrogen and hydrocarbon-loaded nitrogen carrier were alternated. The results of these tests are shown in Table 2. In each test, the retention volume (capacity for) of SF_6 was greater with the pure nitrogen than with the contaminated nitrogen. The retention volume decreased for each member in the series so that, after 5 cycles, the V_R with pure nitrogen was 3040 cc (an 8.6% decrease) and that with added hydrocarbon had declined from 3180 cc to 2610 cc (nearly 18% decrease). Following the 5th cycle, the gas train was switched to bypass the detector and the adsorber was heated to 85°C while being purged with nitrogen for 20 minutes. After cooling, a test cycle was repeated with the V_R for SF_6 being deter-

TABLE 2. EFFECT OF HYDROCARBON MIXTURE ON V_R OF SF_6 ON TYPE AC CHARCOAL AT 24°C

(cc's)

Test Number	Retention Volume (V_R)	
	Without hydrocarbons	With hydrocarbons
1	3325	3183
2	3277	2800
3	3230	2700
4	3135	2688
5	3040	2610
6[a]	3230	3164
7[b]	3495	

[a] Adsorber heated to 85°C and nitrogen purged 20 minutes

[b] Adsorber heated to 85°C and nitrogen purged 30 minutes

mined at 3230 cc with clean nitrogen and 3165 cc with the hydrocarbon mixture present. The adsorber was again heated to 85°C with nitrogen purging for 30 minutes. After cooling, the SF_6 V_R was measured at 3495, seemingly a level of activation greater than that initially indicated.

These data indicate that continuous adsorption of hydrocarbons will definitely lower the capacity for SF_6. By adjusting the quantity of charcoal, however, sufficient sorptive capacity for both can be provided for a single run. For recycle, the hydrocarbons are readily desorbed with the SF_6, thus reactivating the charcoal adsorbers for additional use. In any case, the final version of the sampler contains a presection for the removal of most hydrocarbons.

Passage of the carrier gas through a water-filled gas scrubber to achieve nearly 100% relative humidity did not affect SF_6 adsorption. The V_R of water on the sampler charcoal was found to be only 21 cc, producing an almost immediate, swamping signal from the ECD. Because of the effect of water on EC detection, water was removed from the carrier stream by a short calcium chloride desiccant column inserted between the adsorber and the detector. A series of determinations using this system indicated no detectable changes in the adsorber capacity for SF_6 when collected from a nearly water saturated carrier. This will be discussed in further detail in a later section.

INFLUENCE OF TEMPERATURE ON ADSORBER CAPACITY

Temperature studies were performed through a range of -17°C (0°F) to 71.1°C (160°F). These results are presented in Figure 4. In studying the plot of retention volume vs. temperature, a break is seen to occur between 30 and 40°C. This behavior is markedly similar to that evinced in adsorption isotherm plots wherein a transition from monolayer to multilayer adsorption is indicated. In any case, the diminished capacity of charcoal for SF_6 above 30°C (86°F) clearly established that the weight of adsorbent theretofore used should be increased.

The combined effect of temperature and the addition of the six compon-

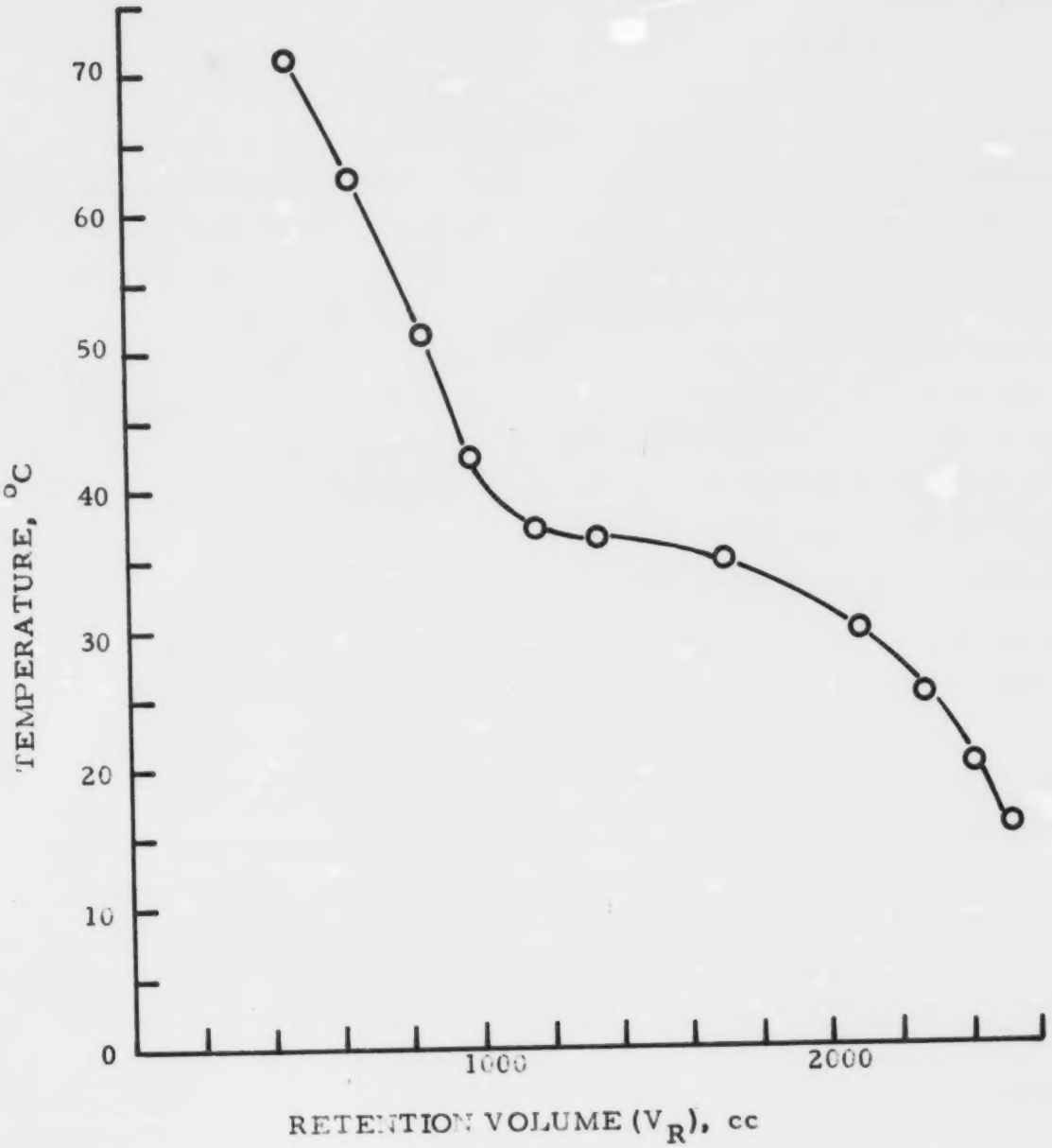


Figure 4. Retention volume of SF_6 on type AC charcoal

ent hydrocarbon mixture was next determined. In these tests, the V_R for SF_6 with pure carrier was compared to that with synthetically polluted carrier (~18 ppm for each contaminant). The V_R values determined (2200 cc at 24°C) agreed with one another within experimental error (2-15 cc variation). After several determinations at increasingly lower temperatures, the V_R at -10°C was still only 2200 cc. Upon warming the adsorber to 25°C, it was found that the V_R had been reduced to only 1150 cc. This indicated that at lower temperatures, the adsorption capacity for hydrocarbons is greatly enhanced to the detriment of SF_6 adsorptive capacity. These low temperature studies supported the conclusion arrived at after operating at elevated temperatures, namely, a greater quantity of adsorbent would have to be provided for in the sampler design.

OTHER ATMOSPHERIC TRACERS TESTED

In addition to SF_6, limited studies of other potential tracers were made. Among these were trifluoromethylsulfur pentafluoride (CF_3SF_5), trichlorofluoromethane (Freon 11), octafluorocyclobutane (Freon C-318) and difluorodibromomethane (Freon 12B2).

Minimal attention was given the first two Freons named because, due to their background levels and physical characteristics, there was a question as to their appropriateness. Freon 12B2 was suggested late in the program and the sample submitted by the National Oceanic and Atmospheric Administration had somehow been compromised such that it was received as essentially an air sample containing only a trace of the Freon.

Dilutions in nitrogen of the above named tracers were prepared in the ppm range. Freon 11 (b.p. 24°C) did not break through after 1 hour at 20°C and a carrier flow rate of 90cc/min (V_R> 75400 cc). At 30°C, the retention volume was 3200 cc and, at 100°C, it was still greater than 2000 cc. Figure 5 displays V_R vs temperature for this material.

Charcoals' capacity for CF_3SF_5 was determined to be greater than for SF_6 throughout the ambient temperature range. This increased capacity is most pronounced at lower temperature, being 50% greater

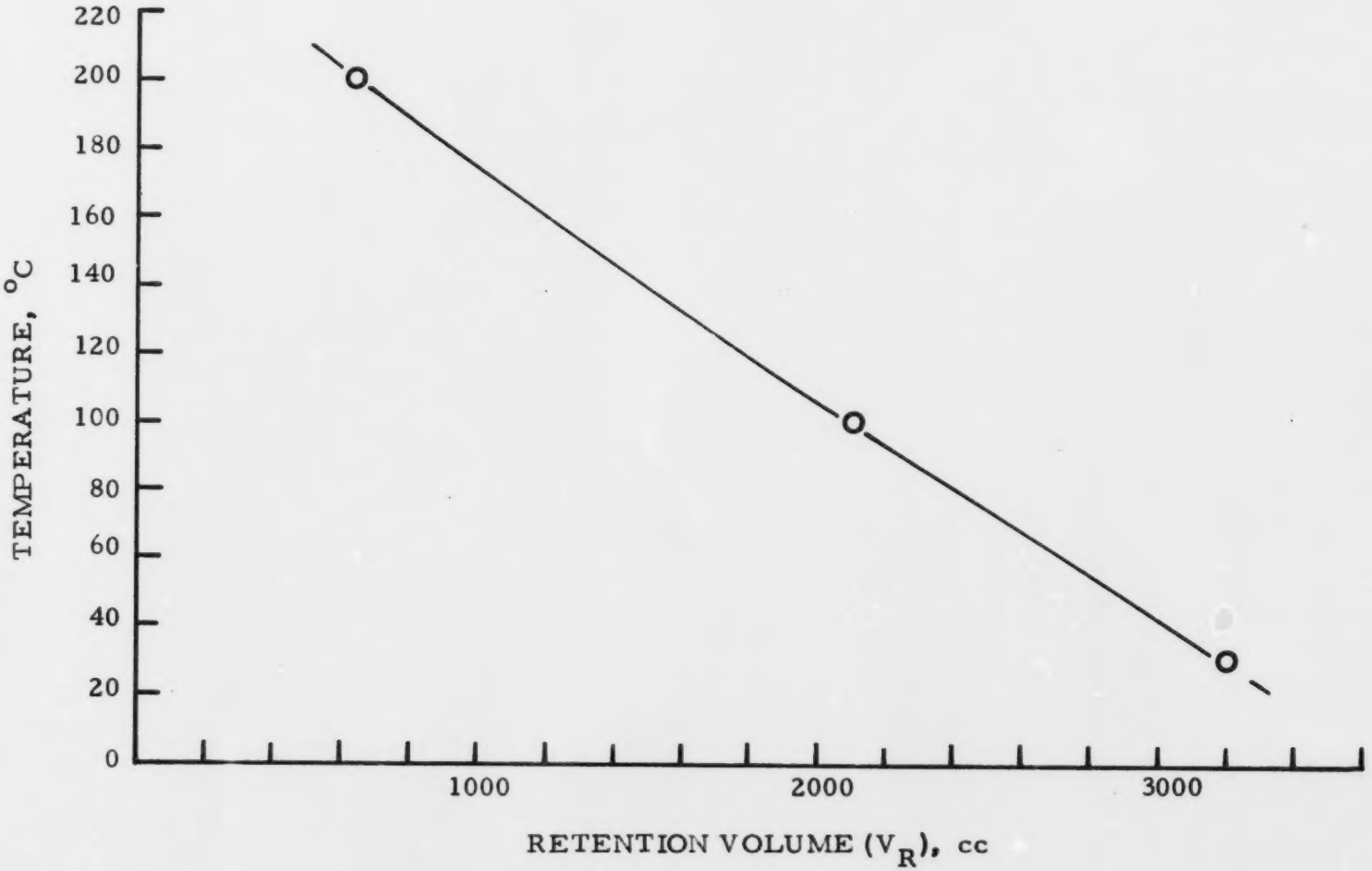


Figure 5. Retention volume of Freon 11 on type AC charcoal

at 20°C. As the temperature is increased, the capacity differential for $CF_3 SF_5$ over SF_6 rapidly decreases to only 5% at 50°C. Table 3 contains a direct comparison of the retention of SF_6 and $CF_3 SF_5$ at selected temperatures on the same adsorber. Figure 6, displaying the retention volume of the latter compound at various temperatures, does not show the sharp break in adsorption at 30°-35°C noted with SF_6.

ATMOSPHERIC TRACERS RESPONSE AND CALIBRATION

The 0.9 ppm (5.4 mg/m^3) commercial mix of SF_6 purchased proved to be too concentrated for determination of response. It was therefore further diluted to 0.9 ppb. A linear ECD calibration for this material was obtained from $5x10^{-11}$ g through $2x10^{-9}$g, as shown in Figure 7. The lower end of the linear segment of the ECD response curve may well extend to less than $5x10^{-11}$g, but this was not determined.

A 1 ppb dilution of $CF_3 SF_5$ was also prepared for ECD response calibration (8.0 mg/m^3). Calibration was carried out only through a range that was required for the laboratory tests. The response was found to be linear within the range of interest ($1x10^{-9}$ g through $2.5x10^{-8}$g), as is seen in Figure 8.

Although these calibrations were performed with a ^{63}Ni electron capture detector, the laboratory also uses ^{3}H radioactive-source ECD'S and a non-radioactive photoionization ECD. Each of these detectors was found to become saturated when sample sizes greater than $2x10^{-8}$gm SF_6 were used. This indicated that no advantages of extended range was available from any alternate type of detector configuration.

ATMOSPHERIC TESTS

The samplers designed for this program will be discussed in detail later. However, the initial version was used for a series of atmospheric tests that are to be discussed at this point. Weather conditions varied from clear, dry, and windy, through dry and still with light smog, through moderate rain. The only problems encountered were with the magnesium perchlorate desiccant used in the sampler. Under humid conditions, it caked and interfered with sample flow. This

TABLE 3. COMPARISON OF THE RETENTION VOLUME (V_R) OF SF_6 and CF_3SF_5 ON ONE LOT OF TYPE AC CHARCOAL AT VARIOUS TEMPERATURES

(cc's)

Temp., °C	V_R	
	SF_6	CF_3SF_5
20	2420	3710
25	2290	3030
30	2110	2460
40	1050	1540
50	880	930

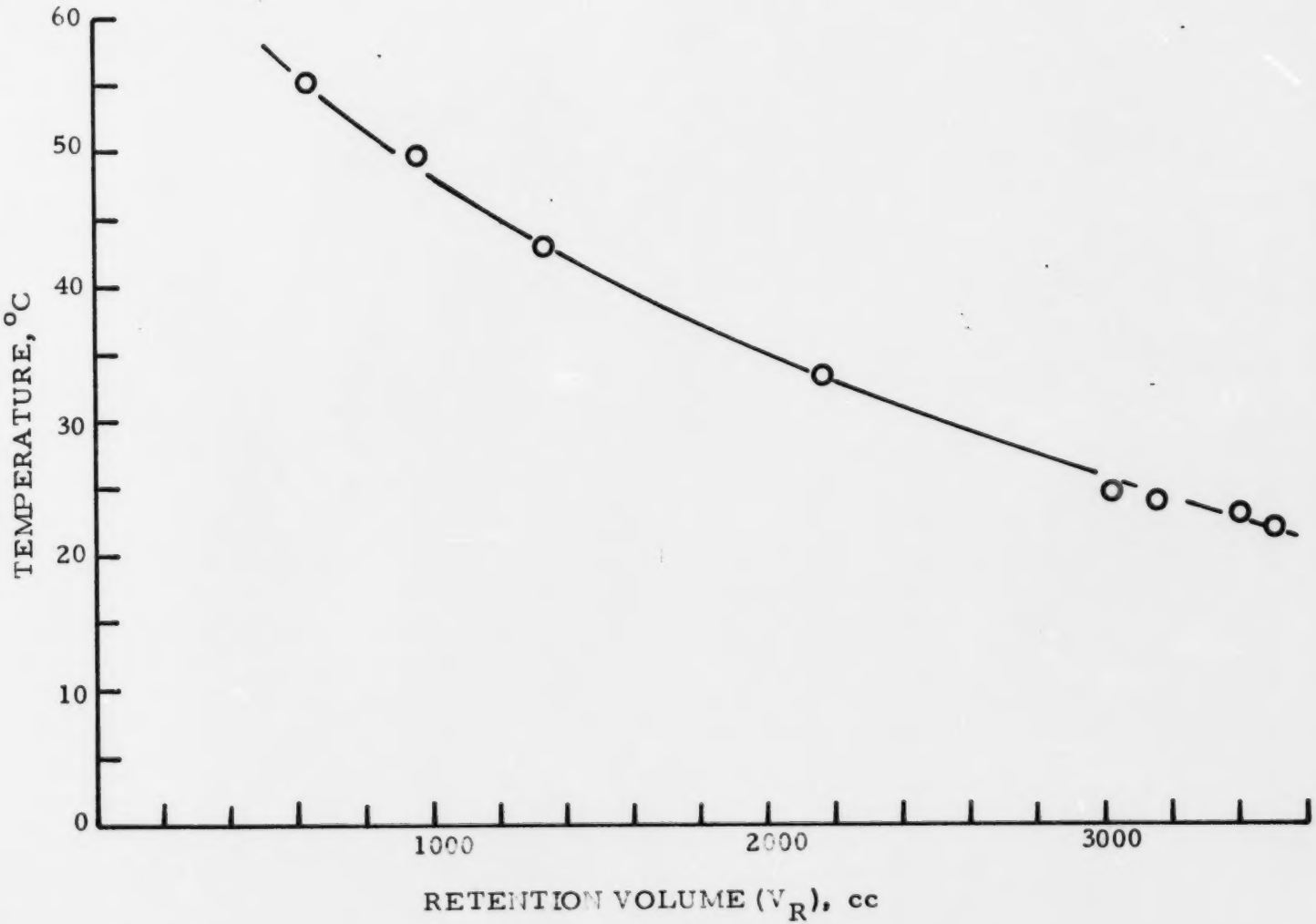


Figure 6. Retention volume of CF_3SF_5 on type AC charcoal

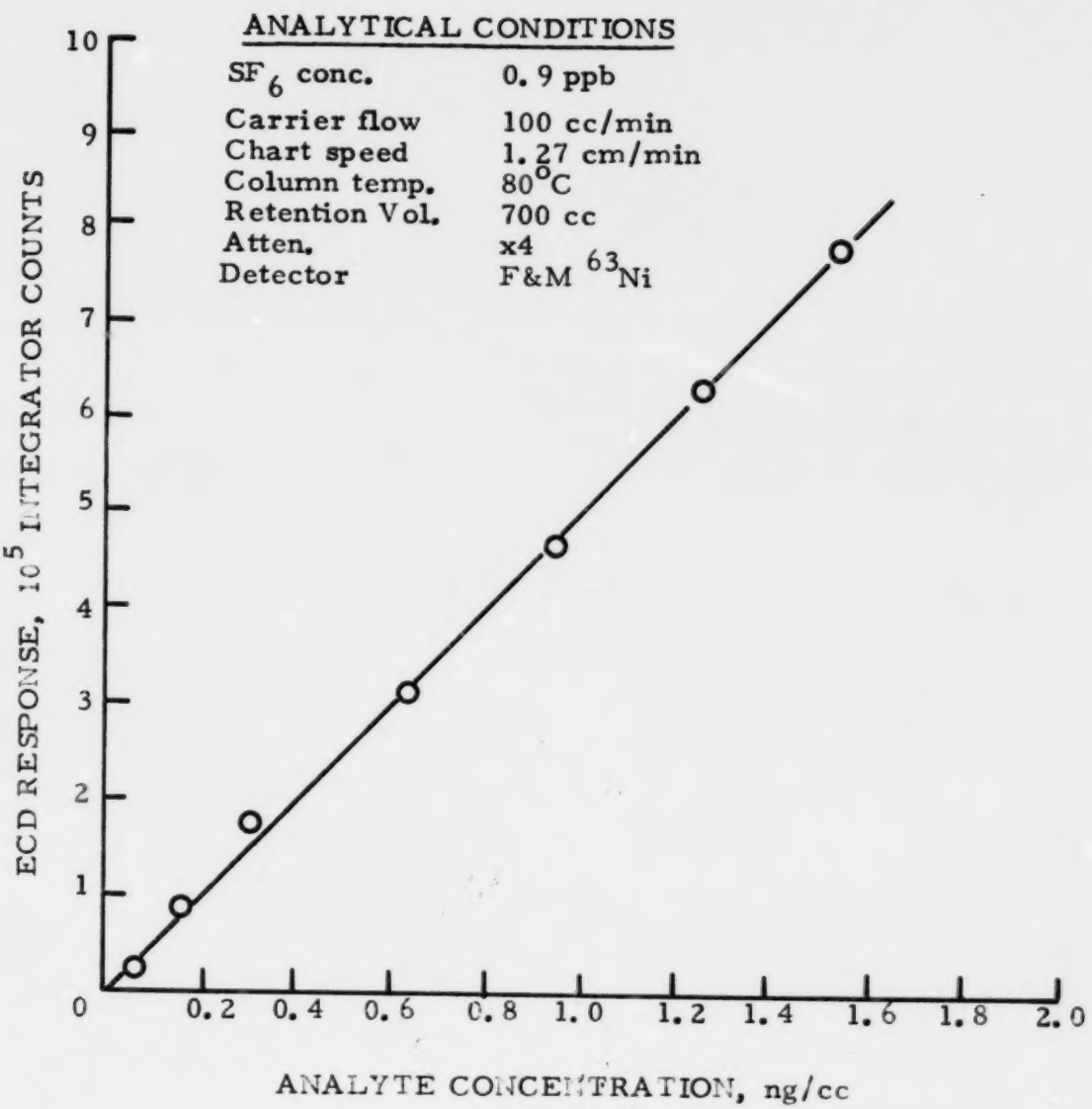


Figure 7. Linear portion of calibration curve for SF_6

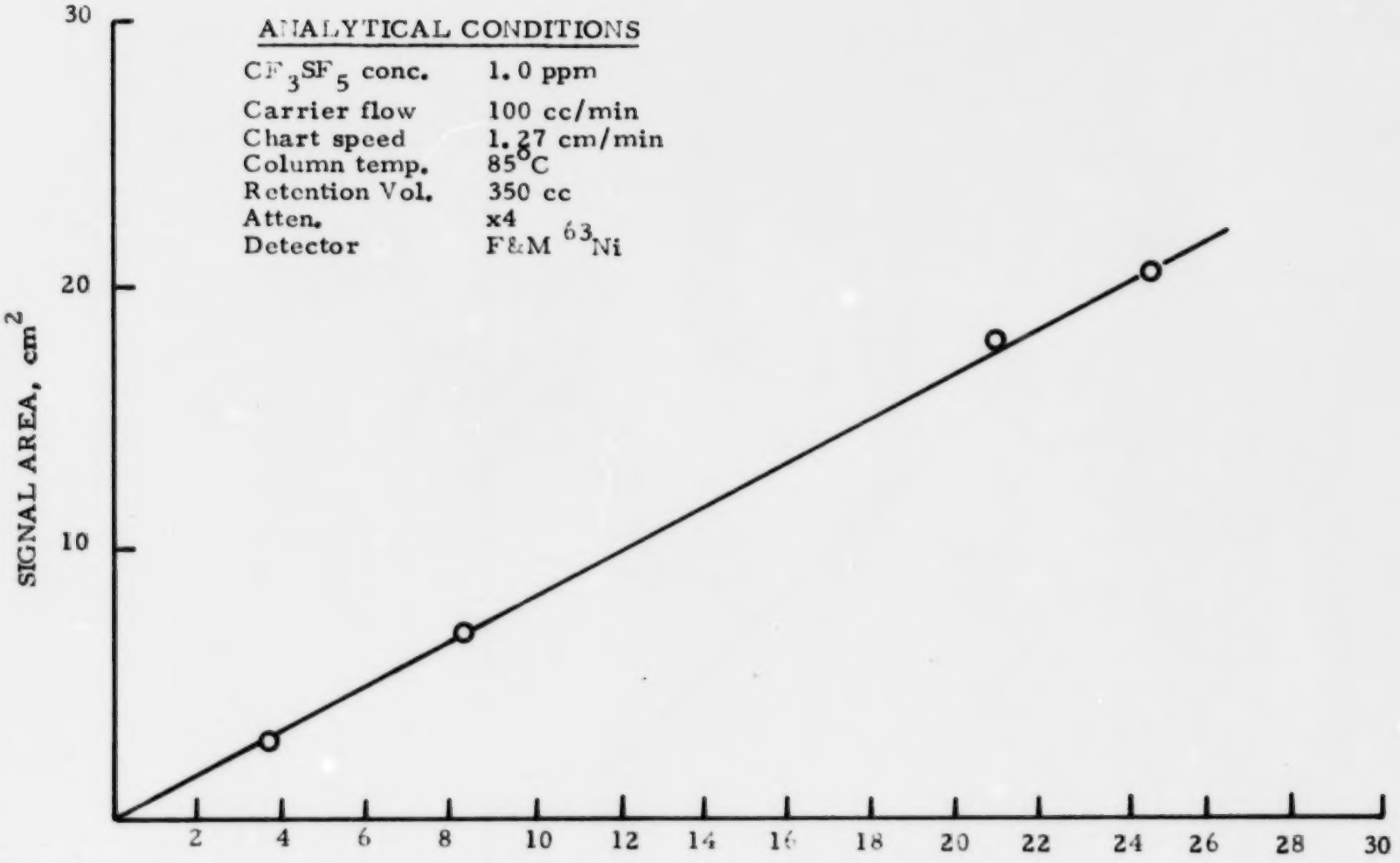


Figure 8. Calibration curve for CF_3SF_5

material was therefore replaced with calcium sulfate which precluded any further problems.

Adding controlled trace levels of SF_6 proved somewhat of a problem, even using a 0.9 ppb mix, but adjustments of technique led to reliable additions. For these tests, the sampler was connected to a vacuum source. The inlet was tee'd, one leg leading to outdoor air. The other leg led to a reservoir of 0.9 ppb SF_6 in nitrogen. Introduction of the dilute SF_6 was adjusted by a flow controller set to deliver 5 cc/min, which is about the lowest practical flow level for these units. The actual flow measured was found to be 5.5 cc/min. The air introduced brought the total flow to 25 cc/min. The density of SF_6 at the temperature of the experiment was 6.5×10^{-3} g/cc, so that SF_6 mass flow was 3.2×10^{-11} g/m.

With flow durations of 15.3, 30.8, and 61.3 minutes, recoveries of 3.4×10^{-10}, 8.6×10^{-10}, and 1.8×10^{-9} g SF_6, respectively, were made, for recoveries of 69%, 86%, and 89%, respectively. Desorptions were performed with a helium purge at 50 cc/min at 150°C for 25 to 60 minutes with cryogenic trapping using liquid nitrogen. As is discussed elsewhere, this method of desorption is not quantitative, vacuum stripping being the preferred approach, as was subsequently employed. The low recovery obtained was not entirely due to the desorption process, however. Another source, which was quickly corrected was a fixed volumetric error. This caused the apparent recovery efficiency to increase with sampling time or volume. Actually the volumetric error was merely being "diluted". This unexpected problem, once identified, could have been corrected for, but a redesign of the dilution system was considered preferable.

The implications of using different types of detectors were evaluated. First, the photoionization ECD was used for a series of samplings as previously described. Recoveries were 83-86%, indicating no major differences from the ^{63}Ni detector.

It is of interest to note that all atmospheric test samples displayed at least 3 ECD signals in addition to that for SF_6, although there were no

interferences (peak overlap) in the analyses. To verify that retained hydrocarbons did not contribute analytical interferences with respect to SF_6 detection, portions of the desorbates from 2 and 3 hours atmospheric testing were passed through a flame ionization detector (FID). Numerous large signals were obtained, but none eluted near the SF_6 or other tracer peaks. Since some ECD's operate over limited temperature ranges, they may become contaminated from condensates acquired over continuous exposure to some higher boiling hydrocarbons. As discussed later, steps were therefore taken to anticipate this potential problem.

The adsorbers used for these tests were subjected to more than 100 exposures to atmospheres artificially contaminated at high levels of concentration. In addition, they were subjected to many hours of urban atmospheric sampling. There were temporary diminutions of sorptive capacity for SF_6 under these conditions, but the capacity was readily restored when the adsorber was heated and purged between tests. The stripping process to remove the tracer from the adsorber will effectively remove any normal atmospheric constituents that would temporarily lessen adsorption capacity.

EFFECT OF CONCENTRATION ON SF_6 ADSORPTION

During long term sampling, tracer concentration over a given time interval will be subject to wide variation. In determining the possible effect upon adsorption capacity, three mixtures of SF_6 at 0.9 ppm, 0.9 ppb, and 145 ppm were connected to a manifold, which was in line of a carrier gas stream, which, in this case, was helium. When the adsorber discharge was connected to an ECD, V_R of SF_6 for any one of or a combination of the SF_6 concentrations could be determined. The flow rates of the tracers were controlled by flow controllers.

Although the lowest SF_6 mixture was 0.9 ppb, the sample was further diluted with the helium carrier in performing these concentration effect studies. In practice, a flow rate of 5.5 cc/min of 0.9 ppb SF_6 tracer into a total carrier flow of 100 cc/min produced an effective concentration of 0.05 ppb.

Altshuller[3] reported from his work that 0.01 ppb is the minimum concentration of SF_6 detectable. This represents an SF_6 mass of 6.5×10^{-14} g/cc. Four orders of magnitude in sample concentration above detectable was the range of sampling capability sought. If six liters of air were sampled, which would correspond to fulfillment of the development objective of sampling at a rate of 25 cc/min for as long as four hours, then the mass of SF_6 to be handled would be 3.9×10^{-10} to 3.9×10^{-6} g.

In the performance of the concentration effect studies, discrete samples were introduced by opening and closing the manifold valving for measured time intervals. Thus, with the flow controller for the 0.9 ppb SF_6 mixture set for 5.5 cc/min delivery, a 5 second sample introduced a mass of 2.4×10^{-12} g SF_6. This is equivalent to sampling, for 4 hours, air having an SF_6 concentration of 6.5×10^{-14} g/cc, the minimum level detectable.

Before each test run to determine the effect of tracer concentration variation, the charcoal was freshly activated by thermal vacuum stripping. Initially, equal volumes of the three SF_6 mixtures were run. This represented a concentration span of 146,000 or five orders of magnitude. The V_B obtained for a 40 second input of a flow of 40 cc/min of each of the mixtures was 3240 cc in each case. Tests were then conducted with the 0.9 ppb mixture diluted in helium to 0.05 ppb to furnish, as described in the previous paragraph, a mass equivalent to that of the minimum detectable level collected over a 4 hour period. Finally, by manipulating the flow inputs from the three SF_6 mixtures, inputs having various concentration patterns, including step-changed ones in which the levels varied by the factor of 146,000 cited above, were effected. In all of these tests, the variations in V_B were small, all falling within a range of 3200 to 3500 cc.

ANALYTICAL SYSTEM

Mention has been made of the column used in the GC system. For analytical purposes, a 50 x 0.32 cm column of the same charcoal as used in the adsorber was employed in the chromatograph. The pur-

pose of this column was to provide separation of the tracer from other electroncapturing materials, and to retain hydrocarbons sufficiently to avoid any possibility of cell contamination. The incorporation of a six port valve in the system permitted easy backflushing once the tracer had passed through the detector. An alternative method consisted of disconnecting the column from the detector and heating the oven to 150-200°C for 15-30 minutes, thus discharging the hydrocarbons into the oven rather than through the detector. Because the sampler itself incorporated a presection of molecular sieve, the need for either procedure was questionable.

The use of a charcoal column does preclude the use of an argon-methane carrier. For the analyses on this program, helium was used as the carrier at a flow of 100 cc/min. Column temperature was 80°C. Five percent methane in argon at 100 cc/min was used as a purge gas in the detector. The analytical instrument was an F & M 5756 chromatograph with a ^{63}Ni ECD operated at 250°C.

Figure 9 shows the response obtained from $3x10^{-10}$ g of SF_6 from a standard mix. Figure 10 shows duplicate runs in which $3x10^{-10}$ g SF_6 was adsorbed on charcoal and desorbed by vacuum-thermal methods, which are discussed later. The chromatograms show considerable peak broadening, which is acceptable in view of the separation advantage gained from the charcoal column. The duplication and recovery are also demonstrably quite satisfactory.

STRIPPING TRACER FROM SAMPLER

The desorption unit initially designed for use with the original sampler is shown as Figure 11. In this photograph, four adsorption tubes are in place. Connected to the two end pieces are an inlet line on one block and an exit line on the other. These allow for purging of the tracer from the charcoal adsorber. To use, an adsorption tube of choice is aligned between the entrance and exit ports of the end pieces. In this manner, the other three adsorption tubes are blanked off. The system is then connected to a helium line inside an oven (an unused

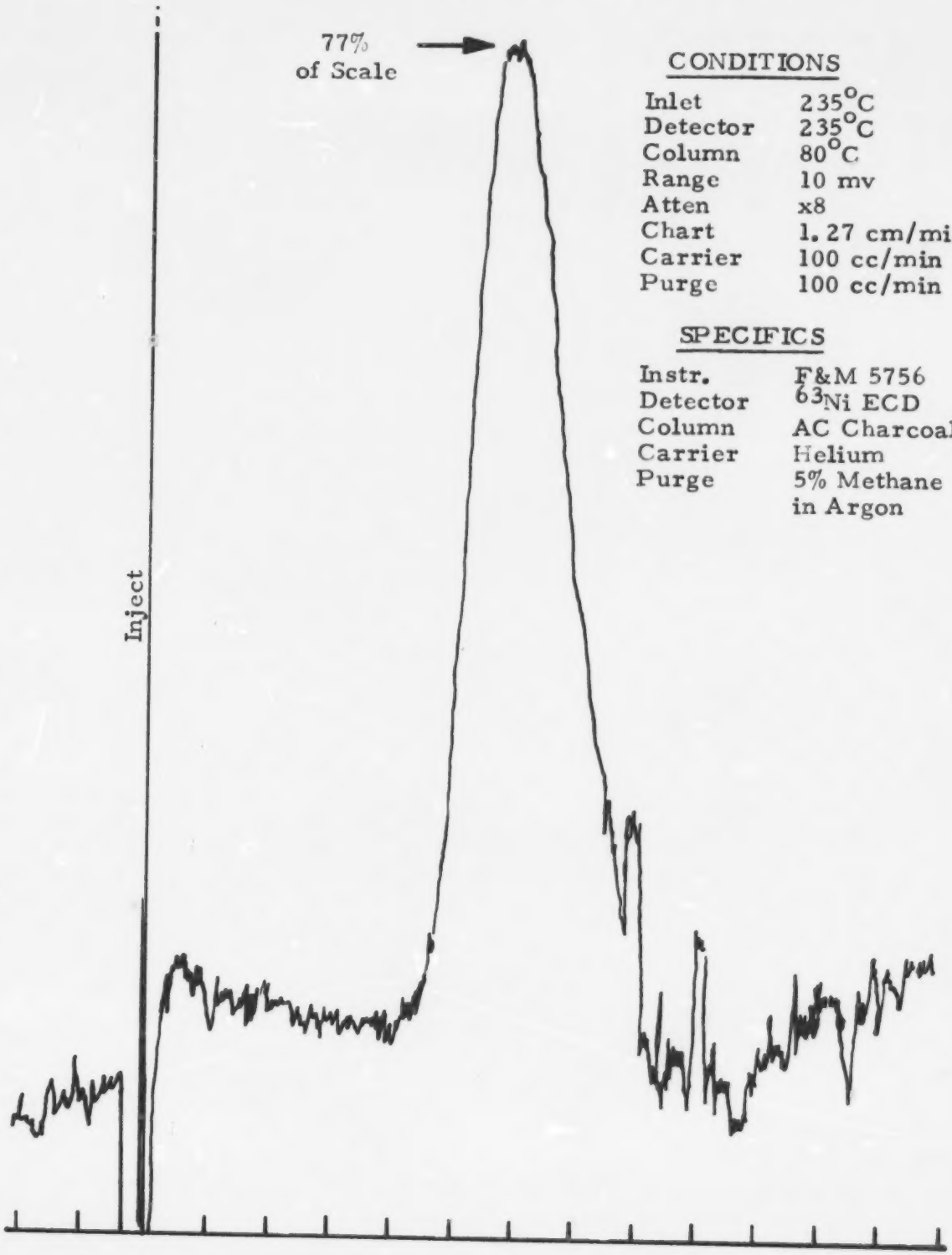


Figure 9. ECD response of 3×10^{-10} g standard SF_6 sample

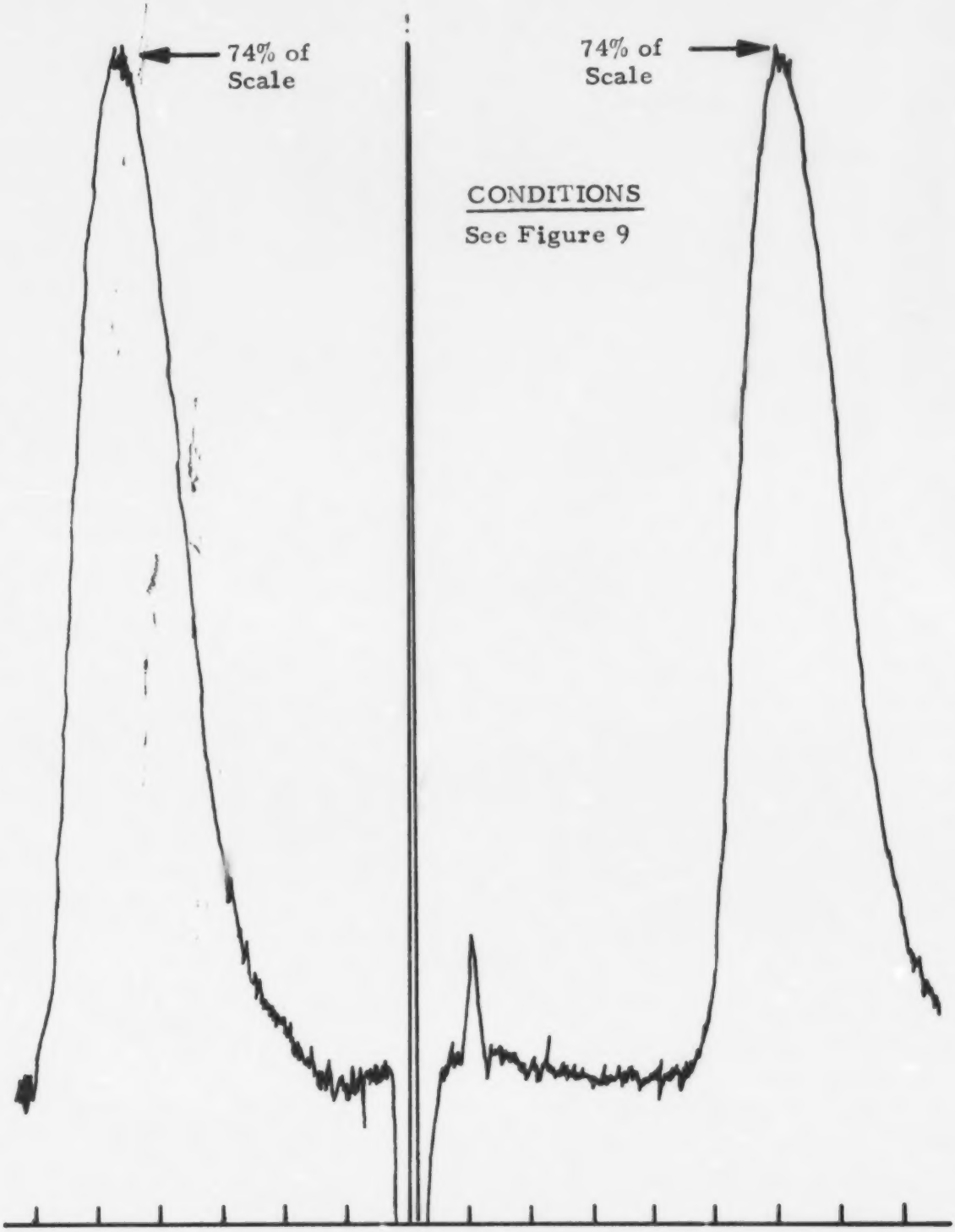


Figure 10. ECD response of duplicate 3×10^{-10} g SF_6 samples following charcoal adsorption-desorption

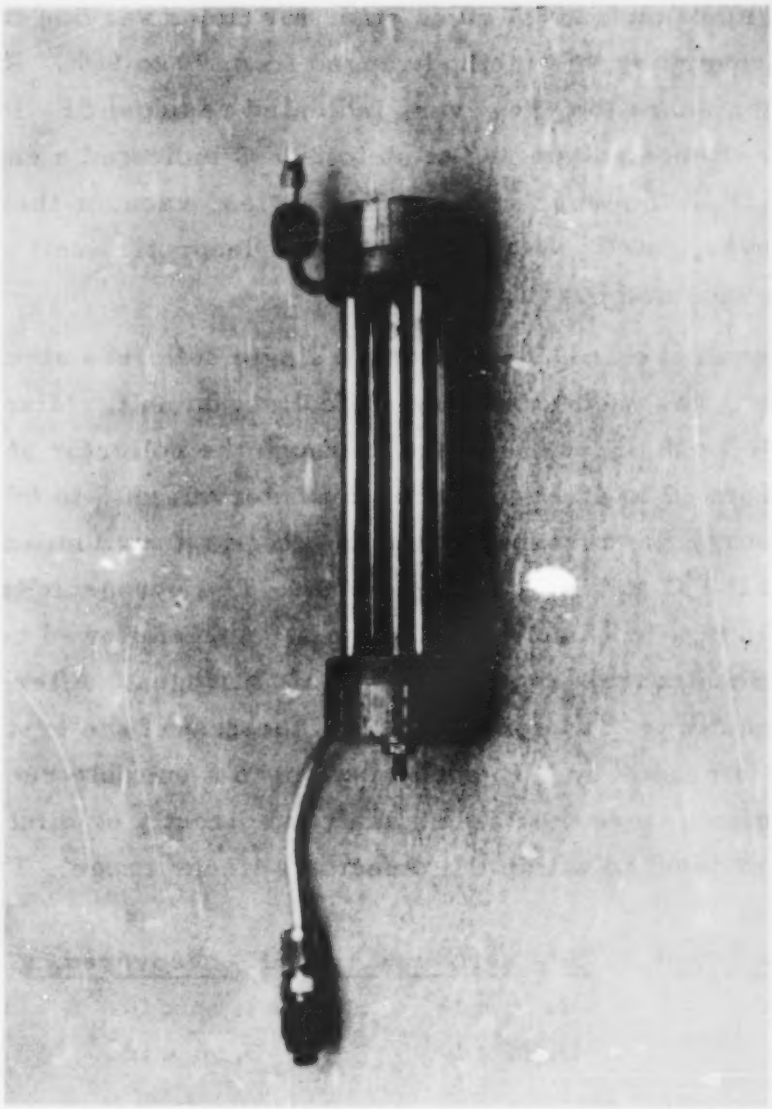


Figure 11. Sampler desorption unit

chromatograph is ideal) and a cryogenic trap system is connected to the exit line. In the present tests, the purging was conducted at 150°C with a helium flow rate of 50 cc/min. for times varying from 25-60 min. Recovery by this method ranged from 70 to 90%. Repeating the desorption operation, however, indicated residual SF_6 in the desorption unit. Repeated purging at up to 200°C indicated a continued residual of SF_6. Because of these difficulties, vacuum-thermal stripping was investigated. Unfortunately, the desorption unit was not amenable to vacuum operation.

To evaluate vacuum-thermal desorption, a single stainless steel tube, 11x0.63 cm, was used to replace the collection unit. Mixes of the 1 ppm and/or 1 ppb SF_6 were passed through the collector at flow rates varying from 20 to 45 cc/min for time intervals of 5 to 60 min. Following exposure, the adsorber was connected to a vacuum rack and desorbed at 150°C at $1x10^{-5}$ torr for 1 hour. The cyrogenic trapping system consisted of a pre-cooler or U-trap at -40°C followed by a high efficiency Schultz trap immersed in liquid nitrogen. After desorption, the Schultz trap was isolated from the rest of the system and its contents transferred (by LN_2 condensation) to a suitable receiver. The trapped contents were then either analyzed directly or diluted to reduce the tracer level to within the detector's linear range. Typical recoveries were:

Concentration added	SF_6 delivered, g	SF_6 recovered, g	% recovery
0.9 ppm	1.76×10^{-6}	1.66×10^{-6}	94.3
0.9 ppb	3.86×10^{-9}	3.66×10^{-9}	94.8

The use of large, high-efficiency vacuum racks for desorption cannot be considered routine procedure for most laboratories. The desorption apparatus was therefore reworked for simpler vacuum stripping. This was accomplished by milling a small recess in both end plates in alignment with the 4 adsorption tubes. By placing a viton 0-ring in each recess, vacuum tight seals were produced when the 0-rings were compressed. The line that had been used to admit the purge gas was plugged. The unit was then placed in a GC oven and the effluent tube

connected to a shut-off valve outside the oven. Two stainless steel traps were then connected in series. Each trap consisted of 3m of 0.32 cm tubing coiled into a 3-loop "race-track" configuration small enough (4 cm x 11 cm) to be immersed in a 250 ml wide-mouth Dewar. Each trap was terminated with shut-off valves on both ends. The first trap was immersed in an alcohol bath maintained at -40°C with dry ice and the second in a liquid nitrogen bath. The loops were situated in the baths so as to pass in and out of the cryogenic liquid. This creates a thermal gradient and flow turbulence such that vapors (and aerosols if involved) are more efficently trapped. The free end of the trapping train was connected to a vacuum pump.

Desorption was accomplished by heating the sampling fixture to 150° and transfering the tracer in vacuo for one hour. This system proved to be only slightly less efficient than what was achieved on the vacuum rack. Recoveries ranged from 80 to 93%. Variations in trapping efficiency, occasionally falling to as low as 50%, were traced to a permanent set of the O-ring seals, which promoted leakage after 2 to 4 desorption cycles. Frequent replacement of the O-rings controlled the problem, and allowed completion of desorption efficiency testing. To enhance reliability, the sampler was redesigned to eliminate the need for O-rings and flat surface seals.

Table 4 contains the data from a series of SF_6 loadings and recoveries using vacuum-thermal stripping with the redesigned fixture. Loading was performed by flowing SF_6 -containing nitrogen at concentrations of 0.9 ppm and 0.9 ppb at carefully controlled rates for varying periods of time through the 4-segment sampler. The test series were generally performed in groups of three since one adsorption tube that had been previously stripped after a preceding test series was included as a control blank. No residual SF_6 was detected from any of these blank desorptions.

Test series 1 through 4 were intended to verify desorption efficiencies in the ranges likely to be encountered in field situations. Tests 5 and 6 were to determine desorption efficiency at arbitrarily selected extremes.

TABLE 4. SULFUR HEXAFLUORIDE DESORPTION RECOVERY DATA

Test No.	SF_6 Adsorbed, µg	SF_6 Desorbed, µg	Recovery, %	Avg. Recovery, %
6A	0.00045	0.00042	93.3	
6B	0.00060	0.00056	93.3	93.3
2A	0.200	0.202	101.0	
2B	0.200	0.198	99.0	99.8
2C	0.200	0.199	99.5	
3A	0.300	0.300	100.0	
3B	0.300	0.307	102.3	100.5
3C	0.300	0.298	99.3	
1A	0.450	0.454	100.9	
1B	0.450	0.443	98.4	
1C	0.450	0.447	99.3	99.8
1D	0.450	0.452	100.4	
1E	0.450	0.450	100.0	
4A	0.600	0.590	98.3	
4B	0.600	0.610	101.6	100.0
4C	0.600	0.600	100.0	
5A	45.0	43.5	96.7	
5B	45.0	45.1	100.2	99.1
5C	45.0	45.2	100.4	

Special care must be taken, when dilution of the trapped tracer is necessary, to insure thorough mixing. A test series in which incoming turbulance and diffusion were depended upon for mixing produced recoveries of only 39 to 43%. The mixing bottles had to be heated and sufficient time allowed for adequate diffusion.

Obviously, insufficient dilution can also produce low results. A test series in which a 45 μg sample of SF_6 was diluted for analyses is cited to demonstrate this. In this series, a 45 μg sample was diluted but insufficiently to enter the linear range of ECD response. The dilution factor can be assigned a relative value of 1.0. Incremental volumetric dilutions of a like sample size are shown to indicate the nonlinear response effect.

NONLINEAR ECD RESPONSE ON APPARENT RECOVERY

Test No.	Relative Dilution	Apparent SF_6 recovery, μg	Recovery
1	1.0	25.3	56.2
2	1.4	29.9	66.4
3	1.7	31.3	69.6
4	2.5	43.5	96.7

These tests demonstrated the magnitude of error that can result from lack of attention to detailed laboratory procedure.

Table 5 contains recovery efficiency of a test series using $CF_3 SF_5$ tracer, in which detector saturation was not involved. The recovery reproducibility was not quite as precise as with SF_6.

SAMPLERS

Figure 12 presents a sketch of the sampler initially fabricated for this program. Figures 13 and 14 are photographs with the adsorption tubes in place and removed. Figure 15 is a display of the desorption system with a loosely assembled sampler.

The sampler unit consisted of 4 stainless steel adsorption tubes, each 11x0.63 cm, evenly spaced around and attached to cylindrical blocks at

TABLE 5. DESORPTION RECOVERY DATA FOR CF_3SF_5

Test No.	CF_3SF_5 Adsorbed, µg	CF_3SF_5 Desorbed, µg	Recovery, %	Avg. Recovery, %
1A	0.150	0.150	100.0	
1B	0.150	0.146	97.3	98.7
2A	0.300	0.290	96.6	
2B	0.300	0.281	93.7	97.0
2C	0.300	0.302	100.7	
3A	0.600	0.586	97.7	
3B	0.600	0.595	99.1	98.4

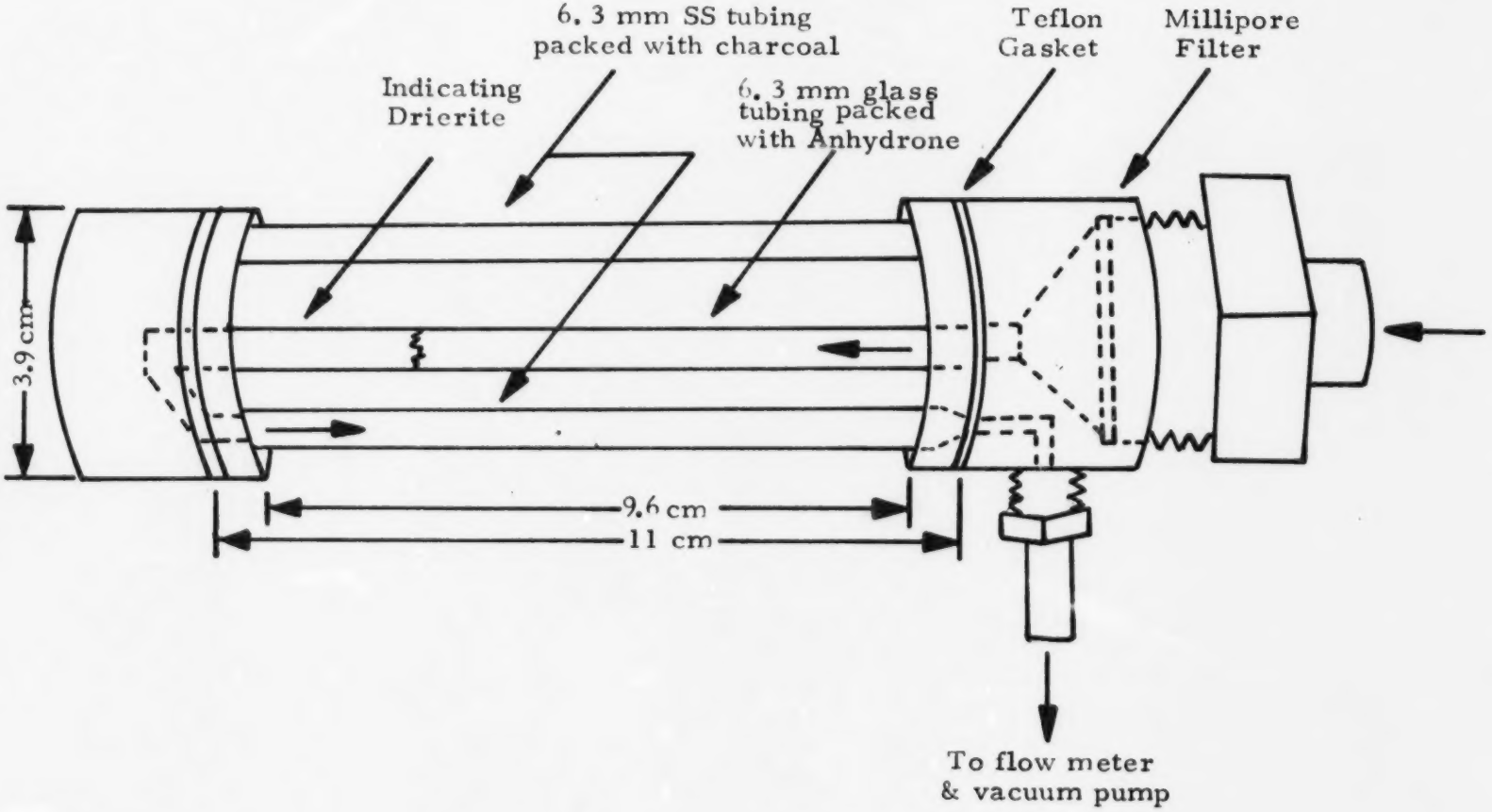


Figure 12. Field-type tracer sampler

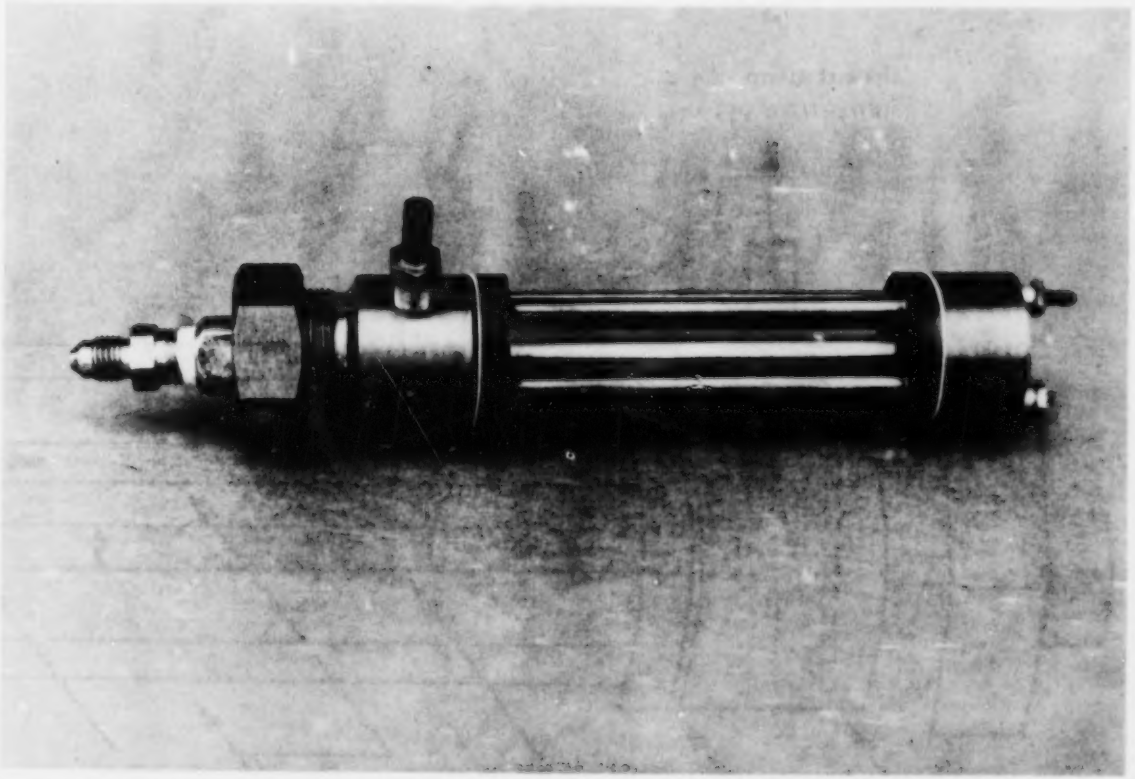


Figure 13. Field-type tracer sampler with adsorption tubes in place

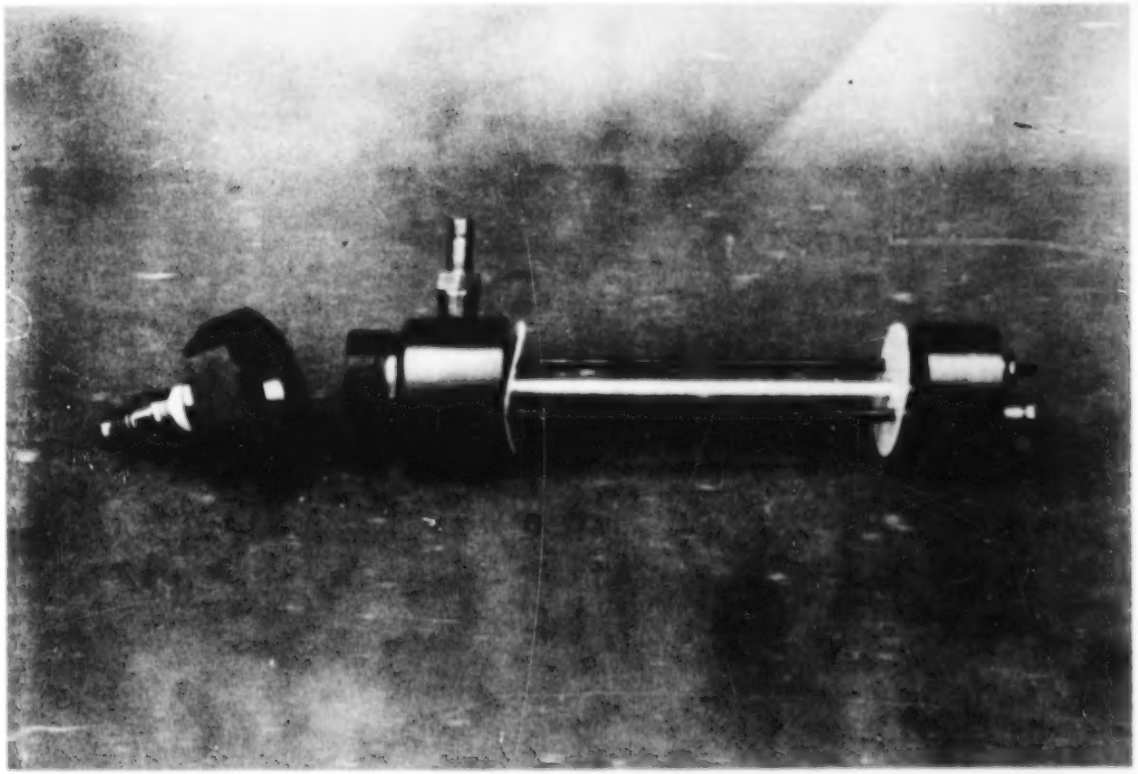


Figure 14. Disassembled field-type tracer sampler with adsorption tubes removed

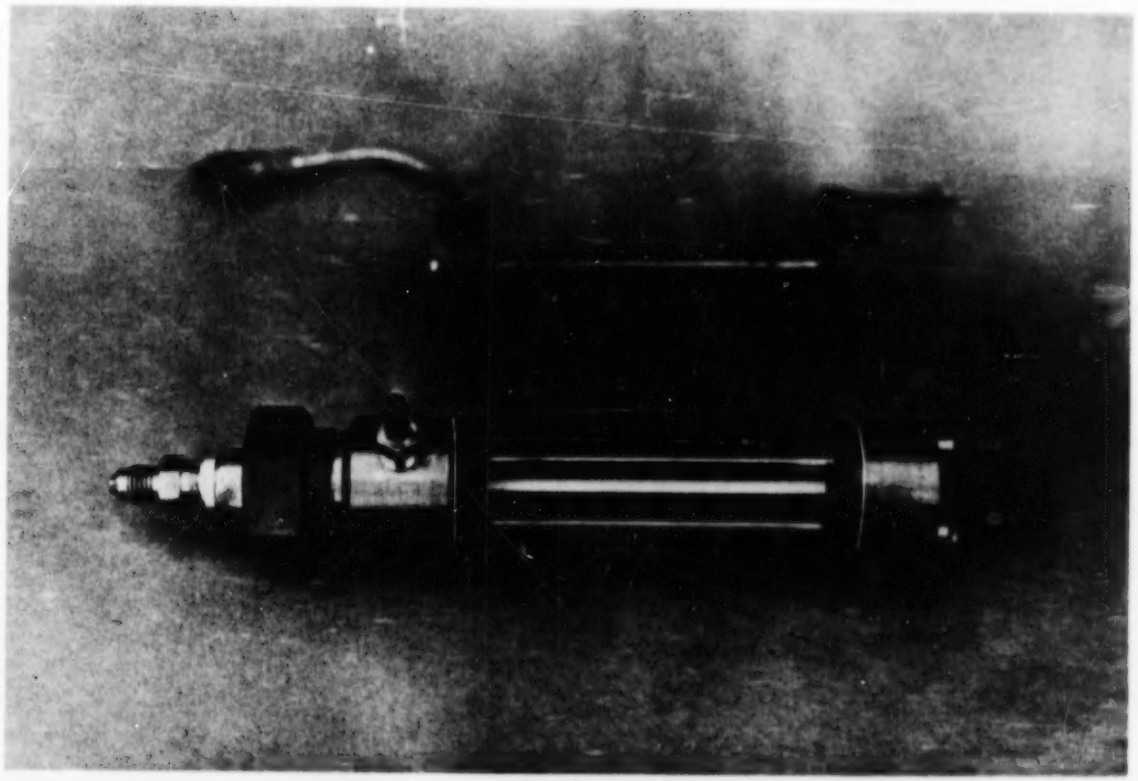


Figure 15. Field-type tracer sampler with desorption unit

either end. Each tube was intended to be an individual adsorber. This assembly was in turn fastened between two larger cylindrical sections which can be called the head piece and end piece. The center of the head piece was bored out and a shoulder milled to accept a standard 25 mm millipore filter with its mounting hardware. The filter was included to remove particulates from the stream sampled. A glass tube, packed with desiccant, runs from the center of the filter recess to the center of the end piece. Ground and screened indicating Drierite proved satisfactory as the desiccant, with the indicator showing when replacement was required.

A side bore in the end piece connected with an opening on the upper surface of the end plate. In the head piece was a similar opening directly over the lower one. This passage led to a discharge opening on the side of the head piece. The end piece and head piece were joined by means of two guide bars which sealed the sampler across teflon discs. In use, one adsorber tube bridged the openings in the head and end pieces, while the other 3 were blanked off by the teflon sealing discs. In this manner, when allowable sampling time was exceeded, or when a change in location was made, the end piece could be loosened and a new adsorption tube moved into line by rotating the column segment.

This design operated satisfactorily and was used in generating much of the data in this report. However, the change to vacuum-thermal stripping created sample recovery problems. These difficulties were discussed previously and, for the reasons stated, a new sampler configuration was designed and fabricated. Figure 16 is a sketch of the essential components. It will be noted that, except for the body of the sampler which is further detailed for machinists' use in Figures 17 and 18, all component parts are standard stock items available in most gas sampling laboratories. The parts used are itemized in Table 6. Figures 19 and 20 are photographs of the sampler with the adsorber and filter holder removed. In Figure 21, the sampler is shown attached to a mass flowmeter in series with a Millipore

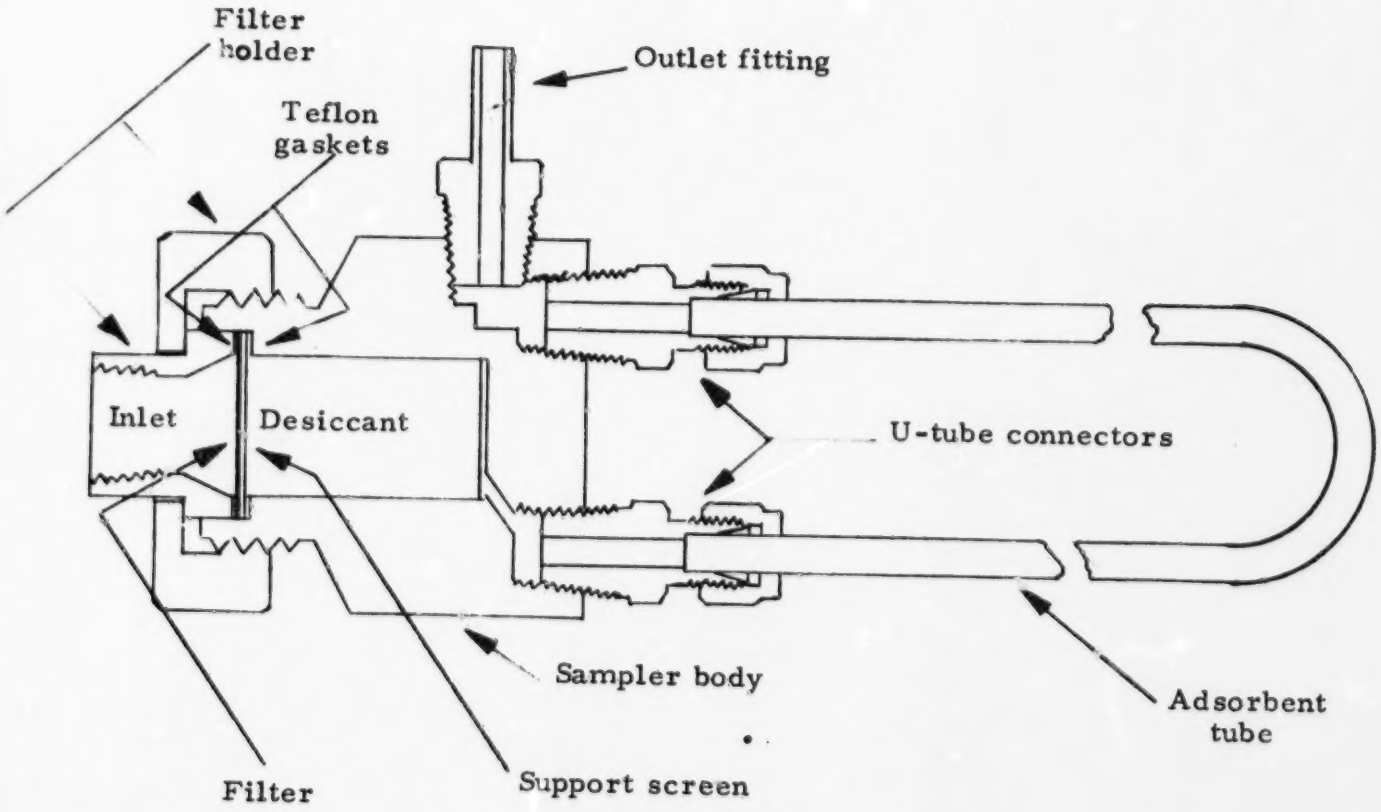
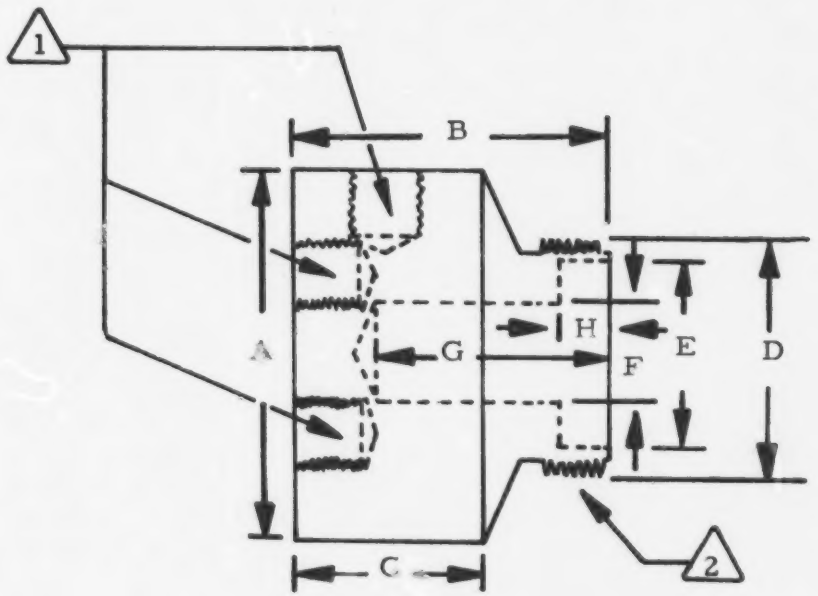


Figure 16. Atmospheric tracer sampler sketch



DIMENSIONS[a]		
Item	cm	in.
A	5.08	2.0
B	4.29	1.69
C	2.54	1.0
D	3.18	1.25
E	2.54	1.00
F	1.43	0.56
G	3.18	1.25
H	0.64	0.25

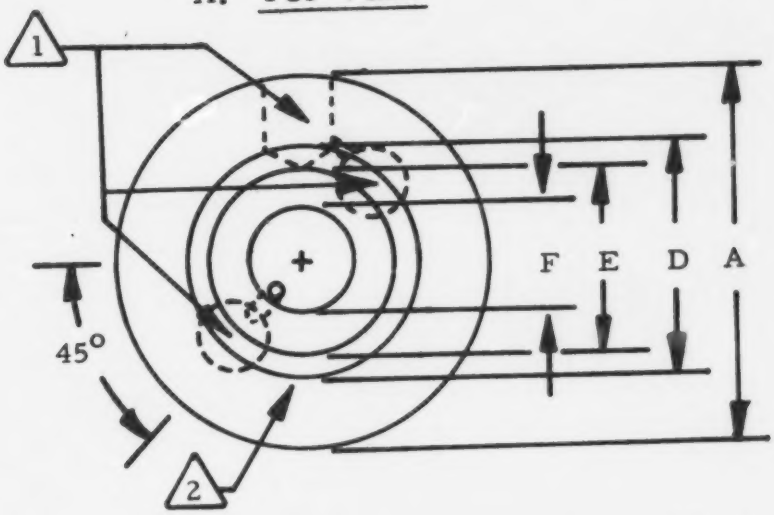
[a] SCALE = 1:1 (Actual Size)

Notes:

1. Drill for 0.25 in. NPT
2. 18 threads/in.

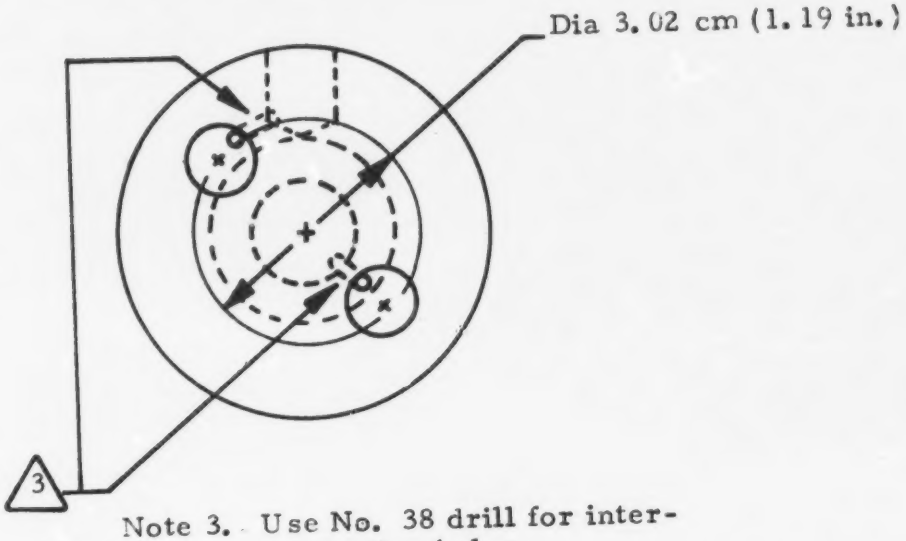
Figure 17. Sampler Body - side view

A. TOP VIEW



Notes & Dimensions per Figure 17

B. BOTTOM VIEW



Note 3. Use No. 38 drill for interconnecting holes

Figure 18. Sampler body - end views

TABLE 6. ATMOSPHERIC TRACER SAMPLER - PARTS LIST

Designation per Figure 16	Manufacturer's Designation	Manufacturer	Manufacturer's P/N
Filter holder	Gas-line filter holder	Millipore Corp.	XX40-025-00 (male portion only)
Filter	MF-Millipore filter	"	RAWP 025-00 (25 mm)
Support screen	same	"	XX66-025-05
Teflon gaskets (2)	same	"	Supplied with support screen
Sampler body	Custom machined	none	See Figures 17 & 18
Outlet fitting	Male adapter, tube to pipe	Crawford Fitting Co.	401-A-2 (brass or SS)
U-tube connector(2)	Male connector	"	400-1-2 (brass or SS)
Adsorbent tube	Handmade	various	See text

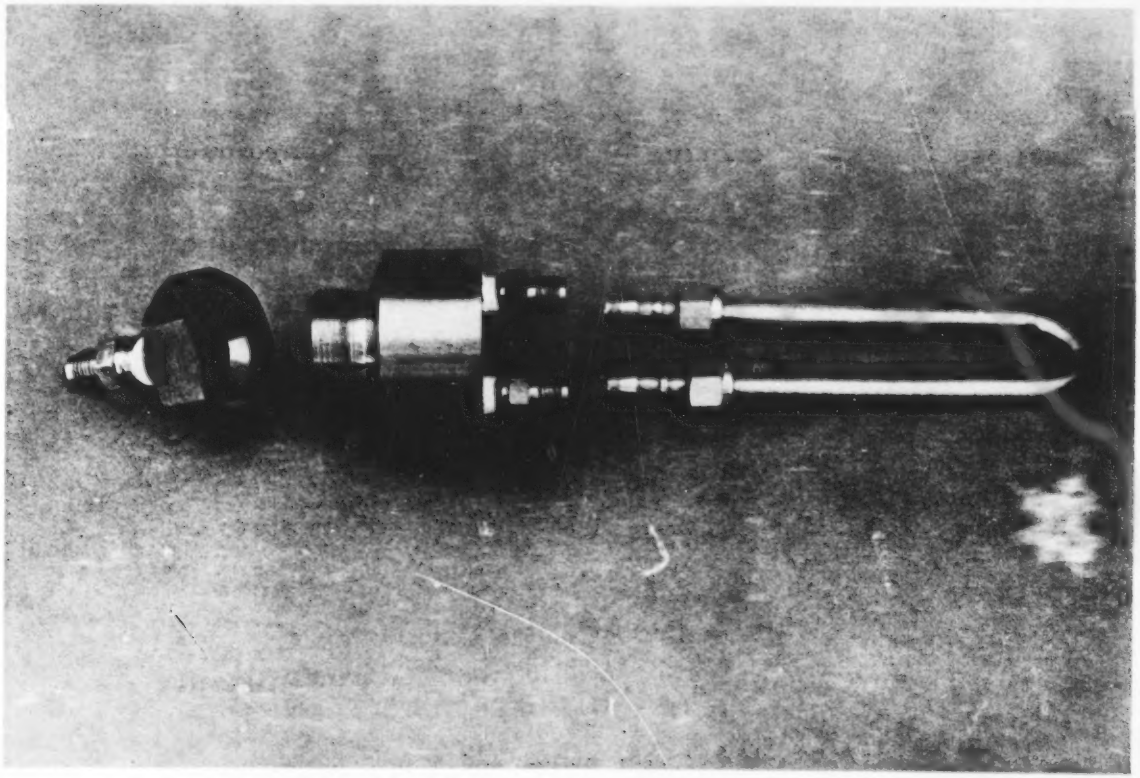


Figure 19. Atmospheric tracer sampler - side-view photograph

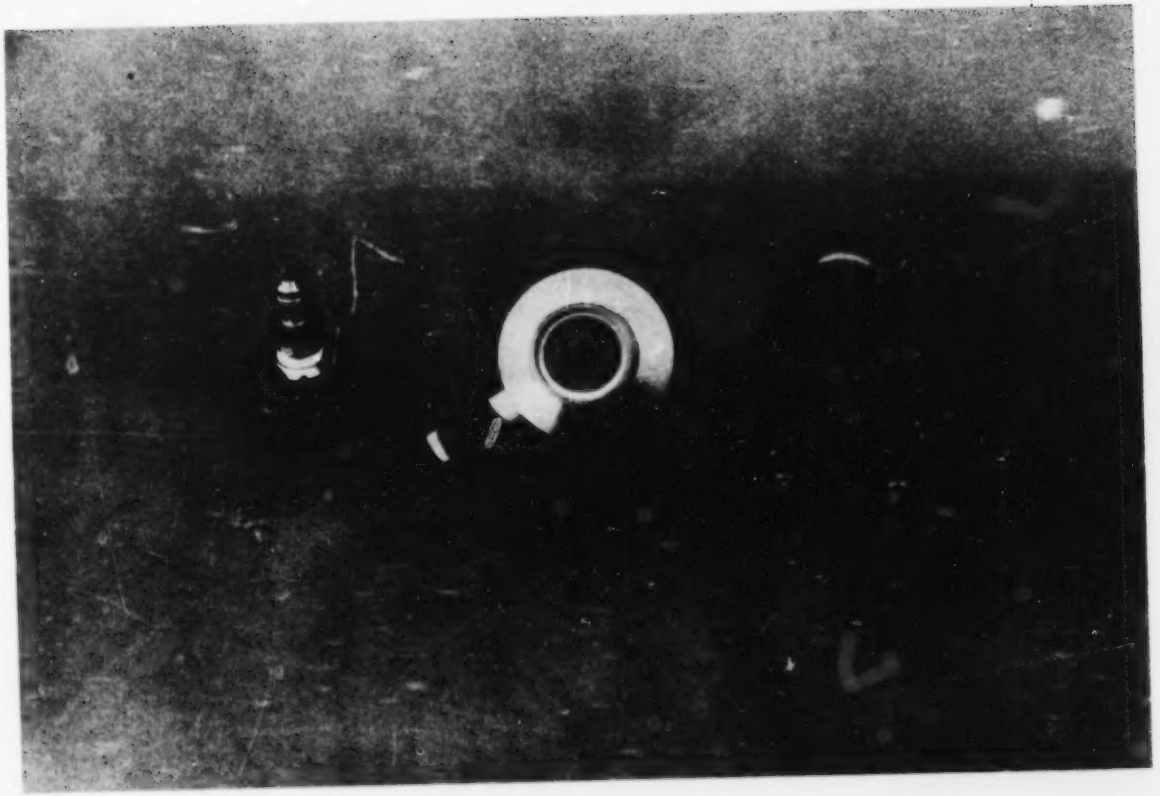


Figure 20. Atmospheric tracer sampler - end-view photograph

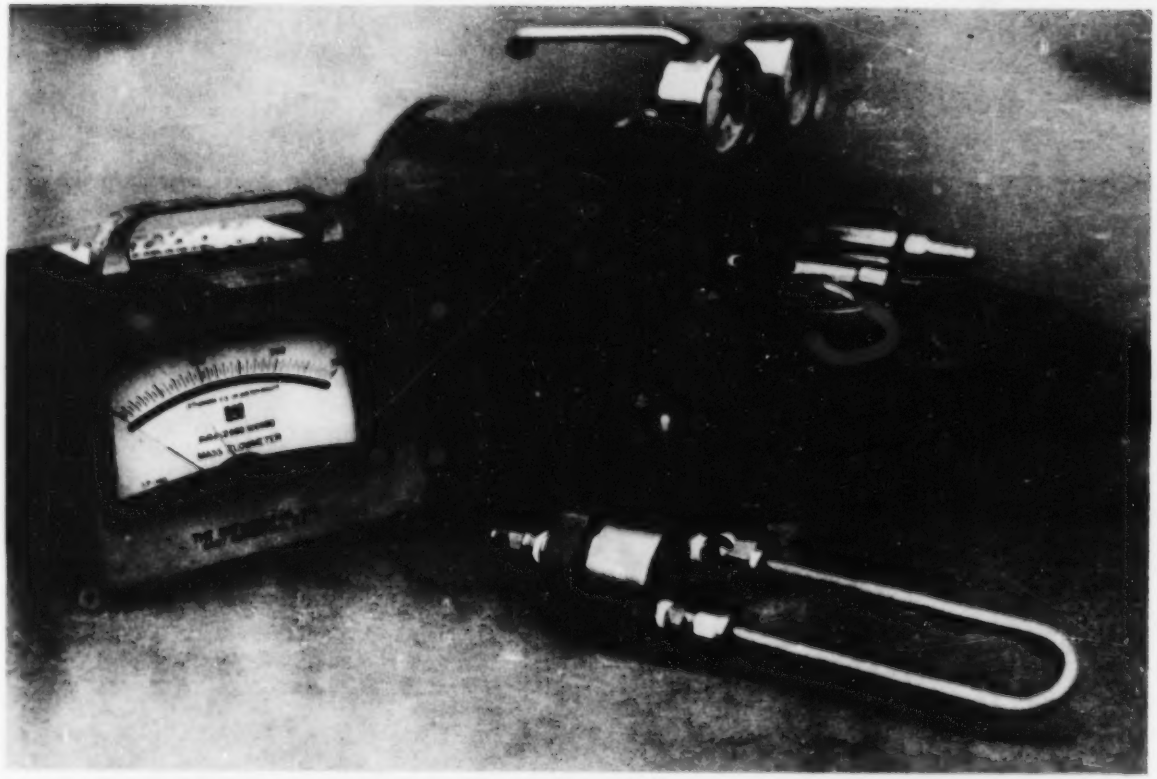


Figure 21. Atmospheric tracer sampler, assembled for field testing

restricted orifice vacuum pump for sampling. This system would be suitable for field use, if AC power were available.

The sampler body was fabricated from a nominal 50 mm (2 in.) diameter rod. The laboratory models were made of brass, although a stainless steel body might prove more desirable for field use. One end of the rod was reduced to 32 mm and threaded to accept a standard filter holder. The center was bored and milled to 15 mm diameter by 31 mm deep. This formed a reservoir for desiccant approximately 5 cc in volume. Above the reservoir, a 5 mm lip was milled out to accept a 25 mm filter, its accompanying stainless steel support screen, and two teflon gaskets. In the bottom of the sampler body, two holes 3 cm apart were drilled and tapped to accept Swagelok 400-1-2 connectors. A 2 mm hole is drilled through one of these latter holes into the bottom of the desiccant receiver. Another hole is drilled at 90° and tapped into the other bottom part. This opening may receive either a Swagelok 401-A-2 adapter or a Cajon 2HN nipple. The adsorber consists of a length of 0.63 cm (0.25 in.) 304 SS tubing bent into a U shape over a 1.51 cm (0.6 in.) radius. The adsorber is packed with 40-60 mesh ground and screened Barneby-Cheney type AC charcoal. The adsorbent is retained by glass wool plugs in either end. The adsorber tube is connected to the two Swagelok 400-1-2 fittings in the bottom of the body. The Swagelok connector is supplied with Swagelok nuts and ferrules, 402-1, 403-1, and 404-1 needed on both the sampler body and the U-tube. The length of the adsorbent tube can be varied with the intended application. For generalized sampling, a 30 cm length is recommended. This will hold $\sim$3 g of charcoal, which, in turn, will adsorb over $\sim$3mg SF_6 when the former is in a moderately active state. With the use of Molecular Sieve desiccant to remove the water and a majority of the hydrocarbons, this capacity should exceed any anticipated atmospheric loading. Filling the desiccant reservoir with 1.6 mm (1/16 in.) pelleted 5A Molecular Sieve provides for water and hydrocarbon removal. By intermingling a few granules of indicating Drierite with the Molecular Sieve, the

need for bed replacement can be detected.

For desorption, the U-tube is removed from the body and the exit-end sealed with a Swagelok 400-C cap. The adsorber is then placed in a suitable oven, with the free end attached to a cryogenic vacuum train as previously described. In most instances it will be necessary to dilute the desorbate to a level that can be analyzed by conventional gas chromatographic means. Sampling rate is recommended at 20-50 cc/min. Tests verifying these recommended procedures were conducted at 25 cc/min sampling rate.

FIELD OPERATION REQUIREMENTS

On the present program, no field testing was attempted or required. The system shown in Figure 21, which was tested only in the laboratory, could be used in the field. The vacuum was obtained from a Millipore vacuum-pressure pump, Cat. Number XX60000 000. The flow was controlled by using a limiting orifice, Cat. Number XX 50 000 01 and adjusting the flow through control of differential pressure by means of the vacuum and pressure regulating valves on the pump. The pump is 38.1 x 20.3 x 21.6 cm and weighs 10.8 kg.

Flow was measured by a general purpose mass flowmeter. A Matheson Model Number 8110-0112 with a range of 0-100 cc/min is ideal for this use. This unit with its transducer weighs 3.4 kg. The meter is 19.7 x 12.7 x 12.7 cm and the transducer, with its connecting cable measures 14 cm high by 5 cm in diameter.

Both the pump and the flowmeter require 115 volts AC, 60 Hz which can be supplied by a small portable generator (0.5-1 Kw), if standard AC is not available.

Before sampling begins, the flowmeter is connected to the vacuum inlet of the pump with its limiting orifice installed. The flow is then adjusted to the desired rate by the vacuum regulator valve. The system is then shut down. The inlet to the mass flowmeter transducer is connected to the outlet of the sampler. The pressure drop through the sampler is so small that only minor adjustment of the regulator valve is necessary

to maintain the preset flow. In fact, because of this, no attempt was made to measure the actual pressure drop, since it would expectedly vary considerably with minor variables of the packing procedure (e.g., the degree of compaction used in inserting a glass wool plug).

It is realized that meteorologists prefer battery operated, low power-draw equipment. It is obvious from the observed characteristics of the sampler that it will be compatible with the small battery-driven gas pumps that are used in the field. An example is the Spectrex pump. This device operates on 6 Volt batteries, uses a potentiometer for flow control, weighs only 225 g, and has a cube volume of only 125 cc. By precalibrating such a pump with a sampler over various time intervals using, say, a wet test meter, it should be possible to field sample in an open loop mode using only the two components and battery power.

SECTION V

REFERENCES

1. Dietz, R. N., and E. A. Cole, "Tracing Atmospheric Pollutants by Gas Chromatographic Determination of Sulfur Hexafluoride," Environ. Sci. Technol., 7, No. 4, pp 338-342 (1973)

2. Turk, A., S. M. Edmonds, and H. L. Mark, "Sulfur Hexafluoride as a Gas-Air Tracer," Environ. Sci. Technol., 2, No. 1, pp 44-48 (1968)

3. Altshuller, A. P., "Atmospheric Analysis by Gas Chromatography" in Advances in Chromatography, Volume 5, Giddings, J. C. and R. A. Keller, Editors, Marcel Dekker, Inc., New York, 1968